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Collection Efficiencies of Stack Sampling Systems for Vanadium Emissions in Flue Gases

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16. ABSTRACT

SUMMARY - An experimental program has been conducted to measure and compare the efficiency of two stack sampling systems to collect vanadium-bearing particulate emissions in flue gas. One sampling system was EPA's Method 5, the other was developed by Exxon Research and Engineering Company for specialized in-house studies.

To evaluate collection efficiency, an extensive factorial study was carried out in a 50 hp four-pass firetube boiler burning typical residual fuel oils. In each test the sampling systems were operated simultaneously in the stack to collect the vanadium-bearing particulate emissions. Three residual fuel oils were tested: two Venezuelan (359 and 149 ppm V) and one Arabian (39 ppm V). A vanadium balance was established for each experiment by inventorying both the particulate emissions and the particulates remaining in the boiler. Test variables, in addition to the sampling systems and fuel oils, also included two combustion residence times and two sampling probe locations.

The results of the study show that vanadium collection efficiency depends on two variables: combustion residence time and sampling system. For both systems efficiency decreases as combustion residence time increases, which results in a particulate size distribution shift to the submicron range. Where particulate emissions are in the coarse size range, collection efficiency in both sampling systems is almost quantitative. The oxidation states of vanadium in fuel oil emissions are briefly discussed.

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*Residual Oil		21B
Flue gases		14B
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COLLECTION EFFICIENCIES OF STACK SAMPLING SYSTEMS FOR VANADIUM EMISSIONS IN FLUE GASES

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1. INTRODUCTION

Studies of vanadium concentration in ambient air have shown a strong link between residual fuel oil combustion and high vanadium levels. There is also growing evidence which suggests that the major part of the vanadium emissions from stationary combustion sources are concentrated in the fine sized particles (1,2). As there are no direct reading instruments for measuring vanadium in stack gases, emission factors for this element must be based on conventional particulate sampling methods, i.e. collecting dust or fumes on filters, electrostatic precipitators and/or impingers. These methods have in common several potential drawbacks:

(1) the possibility that fine particles may not be collected very effectively and therefore pass through the sampling device.

(2) the possibility that volatile vanadium compounds will be lost from the sample by continuously drawing flue gas over the particulate.

The study performed for this contract was to compare experimentally the effectiveness of the U. S. Environmental Protection Agency's (EPA) standard Method 5 particulate sampling train and a stack sampling system developed by Exxon Research and Engineering Company (ER&E) for collecting vanadium emissions in flue gas from heavy fuel oil combustion. The ER&E system overcomes some of the major shortcomings traditionally associated with stack samplers more commonly used. It permits the determination of size distribution of the particulate down to about 0.4 μm and it collects finer particulate in several impingers containing a liquid medium which can operate at stack temperatures. This avoids any possibility that SO_2 will oxidize to sulfate in the impingers which would create false particulates.

To assess collection efficiency of the two sampling trains in a real environment under realistic but closely controllable conditions, an actual boiler was used. The unit consisted of a completely instrumented 50 hp, four pass package boiler manufactured by Cleaver Brooks. For particulate sampling, a platform mounted above the boiler allowed access to two 3" ports which had been drilled at right angles to each other in the 12" diameter boiler stack. Using this arrangement, both sampling trains were operated simultaneously during the tests.

The package boiler burns heavy fuel oil under combustion conditions typical of those in a field installation. The gases moving through the system are cooled in a realistic manner so particulate burn-out and condensation from the vapor phase is realistic. Thus, this boiler is the best equipment of reasonable size for generating particulate approximating those which will be encountered in the field. A large boiler would be too cumbersome in terms of fuel requirements and operating difficulties to carry out such a study under closely controlled conditions.

In order to establish the effectiveness of the collection systems, i.e. their ability to inventory all the vanadium particulate entering the stack, a vanadium material balance was carried out around the boiler. In essence by knowing the vanadium content of the fuel which is burned and determining the amount of vanadium deposited in the boiler, it is possible to establish quantitatively how much of the vanadium particulate is carried into the stack with the flue gas. Since the Cleaver Brooks is a four pass boiler, that is, the combustion products pass the length of the boiler four times before entering the stack, vanadium deposits in each of the passes must be carefully inventoried. Ideally, the firetube, which constitutes pass 1, and the 32 heat exchanger tubes making up the 3 other passes would be completely cleaned out and the amount of vanadium collected would be measured after each run. However, cleaning all the tubes after each run would be extremely time consuming and tedious. To avoid this and at the same time provide a high degree of accuracy, two methods for measuring the amount of vanadium deposition in the boiler were originally proposed. The first involved isokinetically sampling the combustion gases at the end of the firetube. The second involved collecting fallout in stainless steel liners placed in selected heat exchanger tubes in the passes. This latter was selected by the EPA as the most practicable technique.

The amount of vanadium entering the boiler during a given run was determined by knowing the vanadium content of the fuel and the fuel firing rate. This was compared with the vanadium output from a run consisting of: the amount measured in the flue gas leaving the boiler using the sampling systems mentioned previously plus, the amount of vanadium collected in the boiler tubes and passages. In order to measure the latter without going through a long and tedious boiler clean-out after each run, tube liners were used. These were stainless steel inserts which were machined to fit snugly inside certain of the 32 heat exchanger tubes in the four passes. At the end of each run, these liners were removed and the particulates in them were weighed and analyzed for vanadium. The vanadium collected in each insert was considered to be typical of the amount collected in the other tubes in the same pass.

The difference between the vanadium entering the boiler with the fuel, that accounted for in boiler deposits and that collected in the sampling systems gave a measure of the inefficiency of the sampling system and/or inaccuracies in the other measurements involved.

In order to determine how accurate the sampling systems would be over a range of vanadium particulate levels in the flue gas and particle size distributions, runs were made on several fuel oils over a range of operating conditions. The fuels were chosen on the basis that they were typical of those in use now and in the future in the U. S. and that their vanadium contents would span the range which would normally be encountered in U. S. fuel oils.

The primary variable used to adjust combustion conditions was residence time in the combustion zone. Previous (company sponsored) studies by Exxon Research and Engineering Company(3) had shown that increasing residence time decreased total particulate level by burning out carbonaceous particles and shifted size distribution towards smaller particles as the large ones burned out. It was felt that if size distribution had a significant influence on the effectiveness of the sampling systems, it would be primarily because of their inability to collect very small particles quantitatively.

The basic information being sought in this study was (1) what percent of the fuel vanadium was accounted for by the collection systems after correcting for boiler deposits, (2) whether there was a significant difference between the effectiveness of the two systems, and (3) how much the effectiveness changed as vanadium content and size distribution was varied.

Ultimately, four variables were involved in this investigation viz., sampling system, fuel oil, combustion chamber residence time and sample location in the stack. The latter was selected to rule out the possibility that particulate maldistribution in the flue gas would produce a bias in the results. The two sample systems were tested simultaneously in each run using sample ports located 90° apart. A systematic maldistribution might have caused one or the other port to give higher vanadium recovery. A factorial design of the type 2 x 2 x 2 x 3 was used to study the responses of the variables and also provide a framework for analysis and interpretations of the results.

While the factorial program constituted our major effort, some limited experiments were conducted to determine the oxidation state of vanadium particles collected on the filter of the Method 5 sampling train. The methodology consisted of exposing several vanadium oxides to hot flue gas from combustion of a conventional high sulfur fuel oil and then checking for possible changes in the oxidation state.

Prior to the start of the factorial program, a literature survey to assess methods of sampling and analyses of vanadium emissions from combustion sources was made. Sources which were searched included the American Petroleum Institute, Literature and Patents files from 1964 through 1975, NTIS (Government Reports) 1964 through current, and Chemical Abstracts 1970-1975. A bibliography covering this state-of-the-art review is presented in the first Appendix.

2. SUMMARY

Exxon Research and Engineering Company (ER&E) has conducted an experimental study to measure the efficiency of a standard EPA Method 5 stack sampling train to collect vanadium emissions in flue gas and compare it with an ER&E developed stack sampling system. The ER&E system employs an Andersen Cascade Impactor and several high velocity impingers filled with silicone oil. The impactor gives size distribution down to approximately 0.4 microns, finer material is collected in the impingers which now can operate at stack temperature and, therefore do not produce false sulfate type particulate. The stack solids are not soluble in silicone oil so separation of this material is easily accomplished. In these tests the entire sampling system was maintained at 400°F. The full EPA Method 5 sampling train consisting of a probe, a cyclone, a fiber glass filter (MSA-1106BH) and two water impingers were also employed. Sampling was accomplished using the published EPA methodology (4) with the exception that the probe, cyclone and filter were heated uniformly to 400°F rather than the prescribed 225-250°F.

The ability of these sampling systems to collect vanadium emissions was measured in a series of runs on particulates generated by combustion of typical residual fuel oils in a 50 hp four pass package boiler modified to simulate boilers of a variety of sizes. This latter was accomplished by changing combustion chamber residence time. Experimentally, this was carried out by varying the fuel oil firing rate and/or adding an additional section of refractory to the existing combustion chamber. With these procedures residence time could be changed almost 7 fold from roughly 50 msec to 350 msec. In comparison the combustion zone of a large utility boiler may provide a residence time of more than 1 second.

Variables in this study were selected on the basis that they might affect the amount and size distribution of vanadium in the flue gas. Two levels of combustion chamber residence time and three residual fuel oil compositions, which would normally be encountered in the U. S., were chosen. Included were two all-Venezuelan resids with vanadium contents of 359 ppm and 149 ppm respectively and a light Arab resid with a vanadium content of 39 ppm.

An important part of the experimental procedure was the simultaneous operation of both particulate sampling trains during each run. This served to eliminate sampling bias attributable to fluctuations in boiler operation. To accomplish simultaneous sample withdrawal, two sampling ports located 90 degrees apart in the stack were used. As a further precaution, to safeguard against possible maldistribution of particulate in the stack, the sampling trains were systematically rotated between sampling port locations. Thus half of the test program was carried out with a sampling train at one port and the other half with the sampling train at the second port. The selection of sampling port location was accomplished using a restricted randomization.

Ultimately, four variables were involved in this study: sampling system, fuel oil, combustion chamber residence time and sample port location in the stack. To evaluate these factors and provide a framework for statistical analysis, a factorial experimental design of the type 2 x 2 x 2 x 3 was employed. A total of 36 experiments were made consisting of 12 base case runs each with two levels of replications.

The key to evaluating sampling system collection efficiency was a vanadium balance in the boiler. By knowing the vanadium content of the fuel which is burned and by determining the amount of vanadium that deposits in the boiler, it is possible to establish how much vanadium enters the stack. The amount not accounted for in the sampling train represents a combination of collection inefficiency and/or experimental error in measurement and other inaccuracies. Vanadium analysis of the boiler and stack solids was accomplished using Atomic Absorption Spectroscopy.

The amount of vanadium deposited within the boiler was determined by using removable stainless steel liners in one of the heat exchanger tubes in each pass of the boiler. At the end of each run, the tubes were removed and the deposits in each were collected and analyzed for vanadium. Total deposits were estimated by assuming that the vanadium deposited in a liner was equal to the vanadium deposited in each of the other tubes in the same pass. Fire-tube deposits were measured by cleaning the fire-tube after each run. Any vanadium not accounted for in the boiler was assumed to have entered the stack with the flue gas.

The flue gas in the stack was sampled isokinetically using either Method 5 or ER&E systems. Particulate samples from the probe, cyclone, filter and impingers of the EPA system were measured separately and analyzed for vanadium. Particulate samples from the ER&E system were combined into size fractions: >10 microns, 1 to 10 microns and <1 micron. Each fraction was analyzed for vanadium.

For each run the material balance obtained with the EPA Method 5 system was compared with that obtained with the ER&E system. In addition, the material balances between runs were compared to determine the influences of fuel type and vanadium content, combustion residence time and sampling position within the stack. These comparisons were made using analysis of variance.

It was determined that vanadium recovery was dependent on only two variables, combustion chamber residence time and sampling system; fuel type, i.e. amount of vanadium in the fuel, and sampling position in the stack were not statistically significant.

Results obtained with the light Arab fuel oil were very erratic and indicated a high degree of experimental error. This was attributed to the very low V content in the fuel and consequently in the particulate. Vanadium recovery with either sampling train averaged in excess of 100% and ranged between 70% and 174% of the fuel V input. Tests made with this particular fuel could not be used to measure collection system efficiency. In contrast, results obtained using the two all-Ven (Venezuelan) fuels were very consistent and therefore served as the basis for the evaluation.

At short combustion chamber residence time (high fuel firing rate), particulate distribution was predominantly in the coarse size range, total vanadium recovery (boiler plus stack) was highest using the EPA Method 5 system and averaged 88.6 wt. % of the fuel V input. Based on the number and potential inaccuracies of the measurements used to make the overall vanadium material balance (i.e. vanadium deposition in the boiler headers is not accounted for) this value represents nearly quantitative recovery. In contrast, total V recovery using the ER&E system was lower by 7.7% and averaged 81.8 wt. %. This difference was statistically significant (90 percent confidence limit) but still within acceptable limits.

At the short residence time, recovery of vanadium in the fire-tube and boiler passes averaged 29.3 wt. % of the fuel V input or about 34% of the total recovered.

In tests made at long residence time (low fuel firing rate), which by comparison is about 1/3 less than found in a large utility boiler, the particulate distribution was shifted to the submicron size range. This resulted in a significant decrease in total vanadium recovery (boiler plus stack sampling systems) averaging about 21%. This gross change in vanadium recovery, however, is not fully ascribed to collection inefficiency. Part, if not all of the problem, may be caused by the failure to inventory completely the vanadium which deposits in the boiler. At the firing rate used in these tests, the volumetric flow rate of the combustion product gas stream is very low and may produce some maldistribution as it goes through the boiler passes. Since our estimate of the quantity of vanadium sampled in the stack is predicated on the amount recovered in the boiler, it is evident that an error here would distort the recovery value in the stack. Vanadium recovery in the boiler for this case amounted to 22.7 wt. % of the fuel V input, which represents a decrease of 23% compared to the previous tests made at short residence time. On this basis total vanadium recovery using Method 5 averaged 73.9 wt. % versus 62.3 wt. % obtained with the ER&E system.

The difference in recovery between the two sampling systems is real and significant at long residence times. This indicates that V collection efficiency in the ER&E sampling system is lower and is primarily due to the inability of the silicone oil impingers to retain very fine vanadium particles. In contrast, the fiber glass filter used in the Method 5 system has a lower particle size cut-off limit i.e., it retains more of the very fine vanadium particles than do the silicone oil impingers.

The inefficiency of the high velocity impingers to collect the very fine submicron particles was general and not confined to the particular collection medium. In Method 5 several water filled impingers were used as back-up for the filter. Essentially none of the vanadium was found in these impingers even at long residence time where the data suggests that fine vanadium particles were passing through the filter.

Total particulate emissions which were also measured with each sampling system were in reasonable agreement. This was taken as a further indication that only fine highly concentrated vanadium-bearing particulate were being lost through the silicone oil impingers. At short residence time, the two stack sampling trains had total particulate inventories less than 1% apart. At long residence time stack loading was significantly reduced and total particulate inventories differed by about 13%. The higher inventory was obtained with Method 5 and was consistent with the higher vanadium assay.

A variable and highly erratic amount of solids isolated from the chilled water impingers of the Method 5 train were not included in the total particulate inventory. These solids were composed predominantly of ammonium sulfate and ammonium bisulfate and were therefore regarded as artificial particulate, i.e. an artifact of the chilled water impinger system only. The origin of ammonia in the flue gas is not known.

Vanadium collection efficiency of the sampling systems as defined in this study is the ratio of the amount of V collected in the respective stack sampling train to the amount of V in the fuel minus the amount deposited in the boiler $\left(\frac{V_S}{V_F - F_B}\right)$. This presupposes that all losses of vanadium occur from the stack sampling system. Since there is a finite possibility that some of these losses are due to inaccuracies in the boiler measurement, the calculated collection efficiency may be taken as representing only a minimum value. In addition, because of the lower base used in these calculations, collection efficiency is always lower than the corresponding vanadium recovery.

At short combustion chamber residence time, typical of a small boiler, the EPA Method 5 stack sampling train had a minimum vanadium collection efficiency of 83.9%. The ER&E train operated at the same condition had a collection efficiency of 74.3%. At long combustion chamber residence time, typical of a large boiler, where V emissions are mostly in the submicron size range, collection efficiency of the EPA Method 5 system apparently decreased. Collection efficiency amounted to 66.2% compared to 51.1% obtained with the ER&E system.

Several experiments were also conducted to determine the oxidation state of vanadium emissions collected on the Method 5 fiber glass filter. Using selected vanadium oxides and exposing them to flue gas at elevated temperature, it was found that some vanadium (V) was partially reduced to vanadium (IV). Although this is by no means definitive, the results do suggest the possibility that both V^{+4} and V^{+5} emissions may be present in the flue gas.

3. CONCLUSIONS

On the basis of this completed factorial study to evaluate and compare collection efficiency of Method 5 and ER&E type stack sampling systems, the following conclusions can be made:

1. Both EPA Method 5 and ER&E sampling systems show good vanadium recovery at short residence time.
2. Recovery in both sampling systems decreases at long residence time but the decrease was significantly greater in the ER&E system.
3. The EPA Method 5 sampling system generally produced a better vanadium material balance because it collected more of the fine vanadium particles.
4. The Method 5 system collects no fine vanadium particles in the water impingers.
5. The fiber glass filter used in Method 5 has a lower fine particle cut-off size limit than the high velocity Greenberg-Smith type impingers containing the silicone oil or water.
6. The low vanadium content of the light Arab fuel oil made it difficult to obtain a reliable vanadium material balance around the boiler.
7. Total particulate inventories measured by ER&E and Method 5 (front half) sampling trains at 400°F are similar and within experimental error.
8. The back half of the EPA system (water impingers) collects a highly variable quantity of artificial particulate matter.
9. Oxidation states of vanadium emissions in the flue gas may include V^{+4} as well as V^{+5}.

4. RECOMMENDATION FOR FURTHER TESTING

The vanadium material balance measured with the Method 5 train at short residence time probably represents nearly quantitative recovery. The main inaccuracy appears to be associated with the boiler inventory. For example, the amount of particulate fallout occurring at the headers at either end of the boiler is not known. This represents about 10% of the surface area of the boiler and therefore could contribute to the error noted in these measurements.

At long combustion chamber residence time, there is some uncertainty as to how accurate vanadium collection is. The probability that at the low firing rate the combustion gas stream is maldistributed in the boiler passes must rank high. To obtain a better vanadium material balance, i.e., to determine where the losses are, additional efforts may be directed either to improving the collection in the stack or in the boiler. Since the stack sampling train results suggest that very fine vanadium particles are being lost, the chances of collecting them with existing equipment is slight. Therefore primary emphasis in any further testing should be initially placed on improving the vanadium material balance in the boiler.

Vanadium collection in the boiler may be accomplished in several additional tests by two techniques. The first consists of making a complete collection and inventory of all material which deposits in the boiler after a run. While this will be tedious and quite time consuming, it does provide the highest reliability and accuracy. The second employs isokinetic sampling of the fire-tube. While this requires less time to accomplish it, it may also be less accurate particularly if the combustion gases in the fire-tube are maldistributed. Both of these techniques, however, can provide a better and potentially more accurate measure of vanadium particle fallout in the boiler than the single tube insert which was used.

5. BACKGROUND

5.1 Vanadium in the Environment

5.1.1 Ambient Air Measurements

A number of ambient air particulate sampling studies have determined the concentration of specific elements in the collected particulate samples. These surveys have shown, among other things, that the suspended particulate from certain urban areas have significantly higher concentrations of vanadium (V) than corresponding samples from rural areas, or for that matter from certain other urban areas.(5,6,7,8) The highest concentrations, either as fraction of total particulate or $\mu g/m^3$ in ambient air, have been found in cities along the East Coast of the U.S. Measurements in New York City during the 1950's showed annual averages in the range of 2.5 $\mu g/m^3$.(9) Data gathered in 1967 showed that a number of sampling locations in the New York-New Jersey-Connecticut area averaged about 0.5 $\mu g/m^3$ on an annual basis.(8) Other East Coast sampling locations averaged 0.1-0.2 $\mu g/m^3$.This is shown in Table 5.1.

By way of contrast urban areas in the south and midwest averaged .01 to .05 $\mu g/m^3$ of V in ambient air.This level was only a little higher than the V concentrations in rural areas of the same portions of the U.S.

Information of this type on ambient concentration of V particulates has led a number of investigators to the conclusion that the primary source of vanadium in ambient air is fuel oil combustion. Most of the fuel oil used in the United States is burned in the major metropolitan areas along the East Coast, where the highest ambient V concentrations were found. During the period in which much of the data was obtained the fuel oil used was almost exclusively of Venezuelan origin which meant that it had relatively high V content -- about 200-400 ppm by weight -- compared with fuel oils from U.S. or Middle East fuels which usually contain well under 100 ppm V. About 1970 fuel sulfur regulations went into effect along the East Coast, forcing a drastic change in fuel oil composition. A comparison of National Air Sampling Network data on ambient V concentration in 1967 and 1970 for Philadelphia and Washington, D.C. indicates a reduction in level which is consistent with the lower V content of the low S fuel oil, about 50-100 ppm, rather than 200-400 ppm. Many investigators have noted the seasonal variation of ambient V in the areas of high concentration.(9,11) It is highest during the winter months when large quantities of fuel oil are burned for space heating.

	1967(8)	1970 (10)
Philadelphia	.264	.14
Washington, D.C.	.165	.09

The relatively low ambient concentrations of V in midwestern urban areas, indicate that coal combustion is probably not a significant source of V particulates. These areas are as highly industrialized as those on the East Coast, but they use coal as the major fuel. Although many coals contain a certain amount of vanadium, its concentration is low compared with total ash content. Evidently most of the V is retained with the other ash

TABLE 5.1

CONCENTRATIONS OF V IN AMBIENT AIR

YEAR	1967		1970	
	Annual $\mu g/m^3$			
	Avg.	Max.	4th Quarter	Annual Avg
New York, N. Y.	.905	1.4		
Bayonne, N. J.	.445	.99		
Philadelphia, Pa.	.264	.43	.12	.14
New Haven, Conn.	.49	.74		
Washington, D. C.	.165	.23	.09	.09
Chicago, Ill.	.06	.10	.07	.06
E. St. Louis, Ill.	.006	.007		
Hammond, Ind.	.034	.054		
Montgomery, Ala.	.0033	.0033		
St. Louis, Mo.	.0116	.025	.03	
Pittsburgh, Pa.	.016	.034		
Akron, Ohio	.0063	.013		
Phoenix, Ariz.	.0037	.0042		
Denver, Cola.	.0034	.0034		
Dubuque, Iowa	.0062	.0062		
Monroe State Forest, Ind.	.0013	.0017		
Rio Arriba County, N.M.	.0014	.0014		

constituents in the electrostatic precipitators or other particulate collection devices on coal fired combustors.

In areas where low ambient concentrations of V have been found, soil is considered to be the most likely source. On the basis of V/Al ratio Marten et al(12) concluded that soil dust was responsible for a major portion of the V found in large particles in the San Francisco Bay area. They also concluded that fuel oil combustion sources were responsible for V in smaller particles, <1μm.

Size distribution studies on ambient particulates by Lee et al (10) through NASN concluded that where significant amounts of V were found in ambient air, it tended to be considerably smaller than average particle size. Mass median diameter of V particles was 0.5-1 μm vs. 1-3 μm for other particulates. This means that the more of the V particles are in the "respirable" size range, i.e. small enough to penetrate deep into the lungs of a person who might breathe them. Thus if there is a toxicity hazard attributable to V in ambient air, it will be enhanced if a large fraction of the V particles are in the respirable range.

These results mean that size distribution of vanadium particulate is a crucial element in emission measurements. Total emission level does not tell the whole story. A distinction must be made between the vanadium associated with very large particles which settle out rapidly soon after they are emitted and those which are small enough to remain suspended in the ambient air. This same size differentiation also determines the inhilation problems which are associated with ambient particulates. Even during the period when they are suspended in ambient air, large particles don't pose a great physiological problem because they are filtered out in the upper portion of the respiratory tract. However, small particles, <2μm, will penetrate deep into the lungs and may deposit on the surface of alveoli, where there is potential for physiological damage. Thus any method for measuring and controlling particulate emissions or specific components of the particulates must include a determination of size distribution to be truly effective.

5.1.2 Toxicity of Vanadium Compounds

Most of the information on toxicity of V as an airborne particulate is related to industrial exposure to very high concentrations. Boiler cleaners exposed to high concentrations (1000 to 50,000 $\mu g/m^3$) of V_2O_5 dust while removing slag from the tubes of oil fired boilers have shown acute effects to the respiratory system, including coughing and symptoms similar to upper respiratory infection.(9) These effects were not permanent.

Long term exposure to fumes evolved in pelletizing V_2O_5 or in steam cleaning boiler tubes has caused chronic coughing, sputum, wheezing, irritation of mucous membranes, bronchi and infected pharynx. In the early part of this century such exposure sometimes led to tuberculosis which was fatal.(8) With the improvement in industrial hygiene practices, the risk of such exposure has been markedly decreased.

Animal exposures to concentrations of 8,000 to 18,000 $\mu g/m^3$ of V_2O_5 for 2 hours daily for a period of 9 to 12 months resulted in acute and chronic poisoning.(8)

These studies and episodes were all related to airborne concentrations which were order of magnitudes higher than those encountered in ambient air. There is no clear cut evidence that exposure to airborne particulate vanadium compounds at the concentrations normally encountered in ambient air has any acute toxic effects. However, exposures to concentrations of 20 to 900 $\mu g/m^3$ have been related to reduced cholesterol concentrations.

In a statistical study, Hickey et al(13) found a moderate correlation between ambient vanadium concentration and "diseases of the heart" in 25 communities in the U.S. They also found high correlations with bronchitis, pneumonia and lung cancer. However, there was no way of establishing a cause and effect relationship in these studies.

The National Academy of Science has recently completed a study of the health effects of ambient concentrations of V particulates. They concluded that there is no health hazard at the concentrations normally encountered in ambient air. There may be a health hazard associated with high localized concentrations which might be encountered in industries which form or use vanadium compounds, i.e. manufacture of high alloy steel or the suppliers of the vanadium for this use.

5.1.3 Natural Occurrence of Vanadium in Fuels

Vanadium is one of the most common inorganic ash constituents of crude petroleum. Its concentration varies widely according to crude source. North African crudes from Libya and Nigeria are generally very low in V content about 1 to 5 ppm. Middle East crudes tend to be intermediate -- 25 to 50 ppm and Venezuelan crudes tend to be high -- 100 to 500 ppm V. Table 5.2 shows the concentration of V in typical Middle East and Venezuelan crudes and fuel oils which have been used in U.S. fuel oils.

TABLE 5.2

Characteristics of Middle East and Venezuelan Crudes and Fuel Oils(14)

	Lt. Arabian		Kuwait		Tia Juana Med		Libyan	
	Crude	Fuel Oil	Crude	Fuel Oil	Crude	Fuel Oil	Crude	Fuel Oil
Gravity, °API	34.7	15.5	31.4	15.5	26.5	16.3	39.2	22.2
Sulfur, Wt.%	1.7	3.0	2.5	5.0	1.5	2.0	0.2	0.4
Pour Point, °F	-55	+55	-20	+55	-40	+20	+40	+105
Viscosity, SSU @ 100°F	44	-	56	-	116	-	40.5	-
Viscosity, SSF @ 122°F	-	175	-	175	-	170	-	65
Vanadium, ppm	13	37	31	61	156	350	3	10
Nickel, ppm	4	11	7	14	20	31	-	-

The vanadium in these crudes is in the form of organo-metallic compounds which are thought to include many porphorins or porphorin like compounds. A small part of the vanadium is in the form of volatile compounds in the vacuum gas oil boiling range, but by far the most is non-volatile and is associated with the asphaltene fraction. A number of studies have been carried out at Exxon Research and elsewhere in an to characterize this fraction and the organo-metallics it contains.(15,16,17) However, because of its extreme complexity very little separation has been achieved.

Basically, however, the vanadium containing compounds are known to be non-volatile, which means that essentially all of the vanadium in the crude remains in the residual fraction which is normally the basic component of heavy fuel oil. Furthermore, it is primarily associated with the asphaltenes in that residuum. These materials are the most resistant to cracking and volatilization during the combustion process. They form the carbonaceous residue of the spray droplets during the fuel oil combustion process after the volatiles have burned off. These residues, called cenospheres, contain essentially all of the vanadium from the fuel. As the cenospheres burn out in the combustion zone, the vanadium is oxidized, primarily to V_2O_5, which forms the ash residue.(18)

Vanadium concentration in U.S. coal is normally in the range of 15-50 ppm. It is usually in the form of organo-metallic compounds similar to those found in crude oil. The relatively low total V content in conjunction with the high ash content ($\sim$10%) of these coals makes vanadium a minor constituent of the total ash. As indicated in Table 5.3, V amounts to .01-.05% of the ash from coal combustion. As such most of it is removed from the flue gas in the electrostatic precipitators or other ash collection devices. Emission of V particulate from coal firing is only a minor source of atmospheric V as indicated by the low ambient concentrations in industrialized sections of the Midwest where coal is the primary fuel.

TABLE 5.3 (FROM REFERENCE 8)

Concentrations of Vanadium in Domestic Coals

Coal Source	Vanadium in Ash %	Vanadium in Coal ppm
Northern Great Plains	.001 - .058	16
Eastern Interior Region	--	35
Appalachian Region	--	21
Texas, Colorado, N.Dakota, S.Dakota	0.01 - 0.1	--
West Virginia	0.018 - 0.039	--
Pennsylvania (Anthracite)	0.01 - 0.02	--
Buck Mountain Bed	0.11	176
Diamond Bed	0.09	92

5.2 Nature of Vanadium in Emissions

5.2.1 Mechanism of Particulate Formation

Fuel oil is sprayed into the combustion zone of a boiler in the form of 100 - 300 μm droplets which are mixed with combustion air as they enter the flame. Single droplet studies have given a good picture of what happens to the droplets in the combustion zone. As the droplet heats up, the volatile materials boil off, especially those in the outer layer and burn in the vapor phase. This leaves a shell of non-volatile solid material around the surface of the droplet. As the droplet temperature increases, volatile material from the interior of the droplet vaporizes and ruptures the outer shell, leaving holes in it and forming a solid layer further in. This process is repeated until all of the volatile material has vaporized and as much of the non-volatile material as will crack into volatile hydrocarbons has done so. This leaves a solid, carbonaceous residue roughly the size of the original droplet but containing a high percentage of void volume. This residue is called a cenosphere. Most of the material in the cenosphere is the asphaltene fraction of the fuel oil. We have found that the asphaltene content of a fuel oil is a very accurate predictor of the amount of cenosphere which will be formed during combustion, and of the total weight of stack solids which will be emitted at a given set of combustion conditions. Figure 5.1 shows electron microscope pictures of cenospheres which are >10μm and Figure 5.2 shows partially burned out material in the 1-10μm.

Since essentially all of the vanadium in the fuel is contained in the asphaltenes, it will also remain in the cenospheres. When the cenospheres form, most of the vanadium is still in the form of organo-metallic, porphoryn-like compounds. As the cenospheres burn out, the vanadium is converted into the oxide form. No studies are available to tell what oxide is present in the partially burned out cenospheres, but after complete burn out, V_2O_5 is formed at combustion conditions. Almost all of the cenospheres do burn out before they leave the combustion zone. The asphaltene content of a typical high S (2.2%S) Venezuelan fuel oil is 10-12%, whereas total particulate emissions from a well run boiler are less than 0.1-0.2 wt.% on fuel.

When the carbonaceous portion of the cenosphere burns out, the V in the ash residue tends to form V_2O_5. Figure 5.3, which is from reference 19, shows the equilibrium between V_2O_4 and V_2O_5. Increasing O_2 content favors the formation of V_2O_5 but increasing temperature favors V_2O_4 formation. At normal combustion conditions significant V_2O_5 formation is favored. Under combustion zone conditions, V_2O_5 has a significant vapor pressure, as shown in Figure 5.4, also from reference 19. It is high enough so that all of the V present even in the highest ash fuel oil can be vaporized. As the combustion gases move through the heat exchanger sections of the boiler, they are cooled and the vapor pressure of V_2O_5 drops. Particulate V_2O_5 forms. The bulk of it is in the very small size range because of the rapid cooling rate. When the gases leave the boiler at 5-600°F or less, the vapor pressure of V_2O_5 is low enough so that only a negligible amount is in the vapor phase. Vanadyl chloride VCl_4 which boils at 300°F has a vapor pressure, and would be in the vapor phase in the flue gas. However, no one has reported any formation of VCl_4 in the combustion of fuel oil.

Thus vanadium particulates in the flue gases leaving a boiler are distributed over the entire range of sizes. The cenospheres which are 10-50μm in diameter contain vanadium in the carbonaceous matrix; partially burned out cenospheres in the 1-10μm range contain a higher percentage of V; and submicron particles of V_2O_5 are formed by condensation from the vapor phase.

FIGURE 5.1

>10 MICRON PARTICULATE EMISSIONS
(CENOSPHERES)

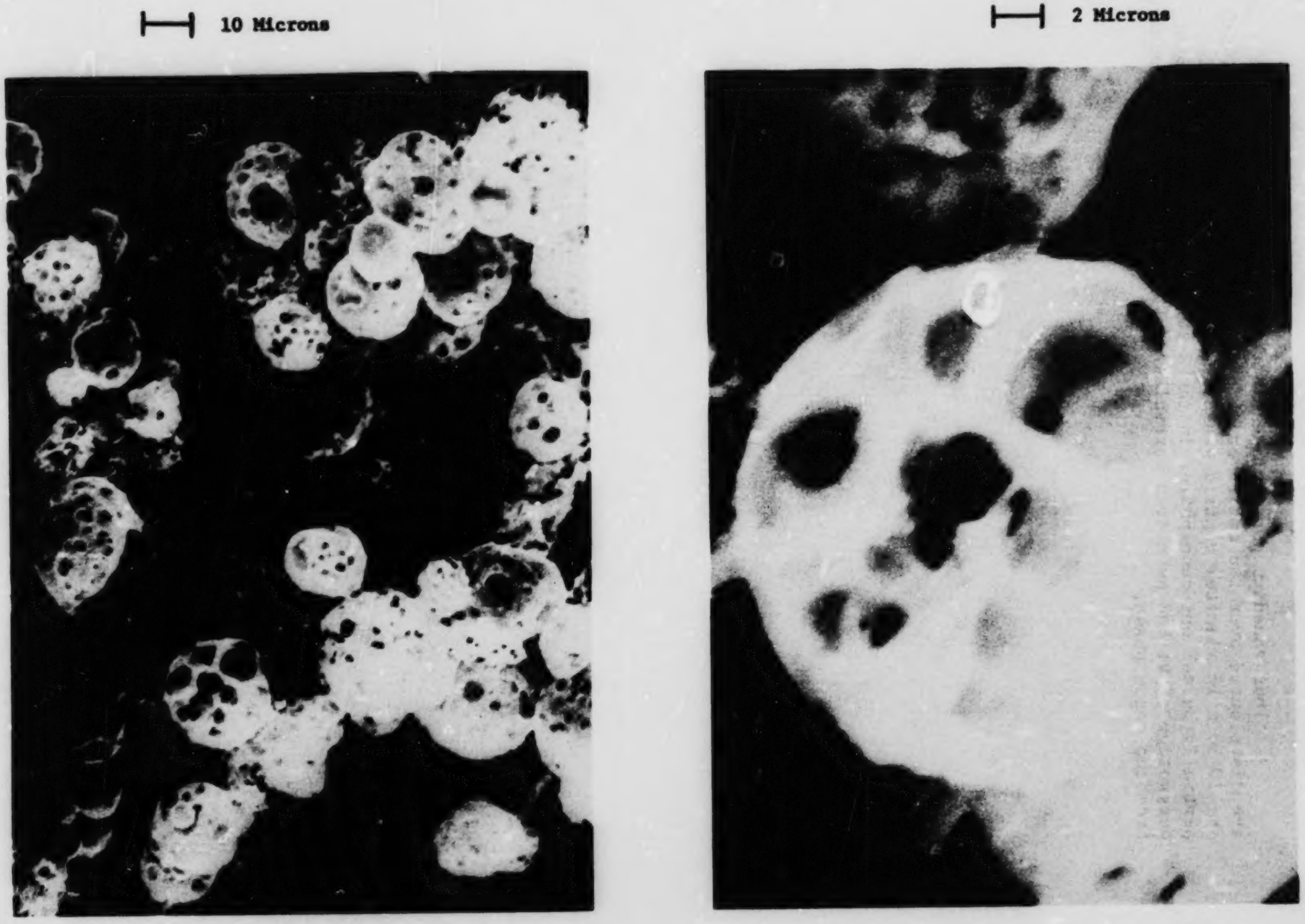
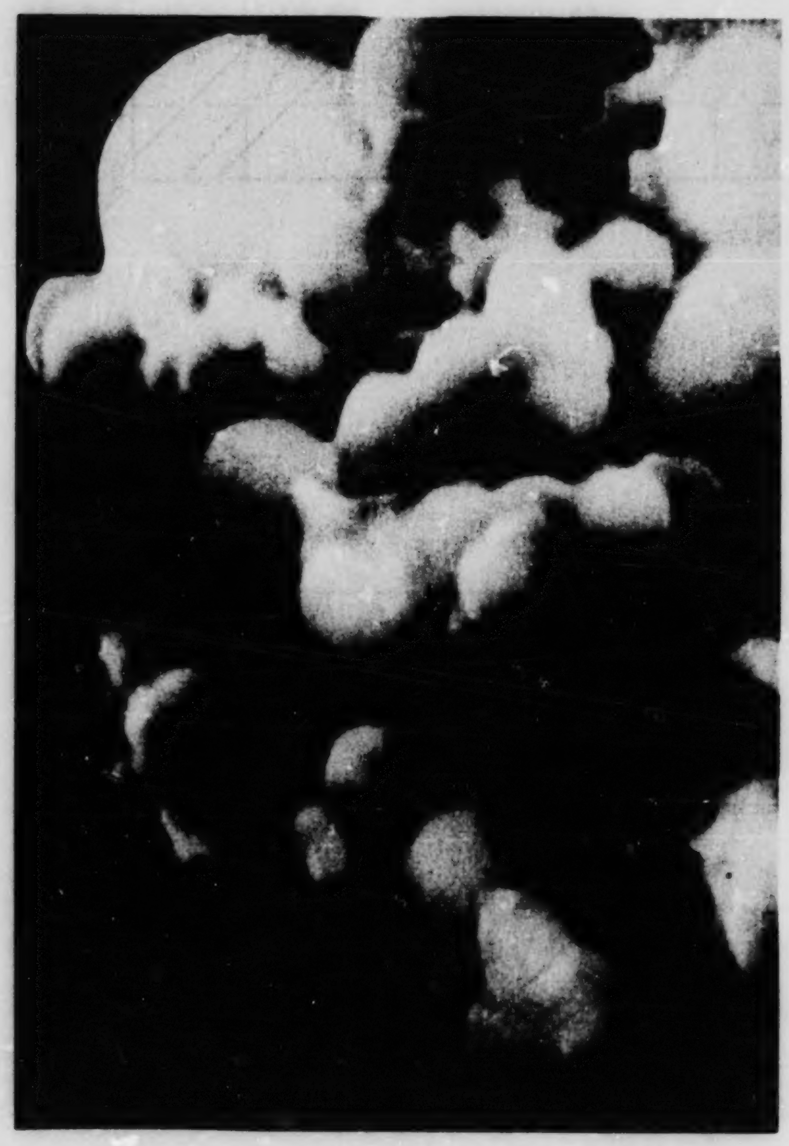

10 Microns
2 Microns

FIGURE 5.2

INTERMEDIATE SIZE RANGE (1-10 MICRONS) PARTICULATE



├──┤ 1.0 Microns

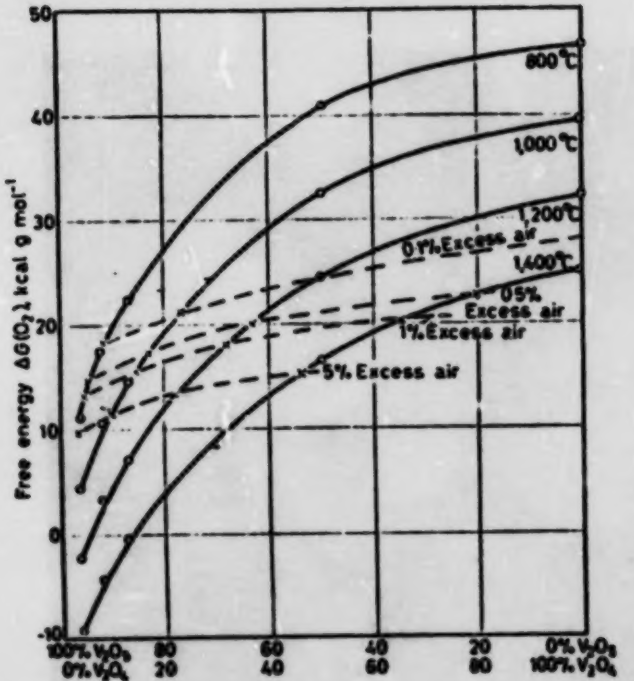


Fig. 5.3 . The effects of temperature and oxygen availability on equilibrium composition for the reaction $2V_2O_5 \rightleftharpoons 4VO_2 + O_2$

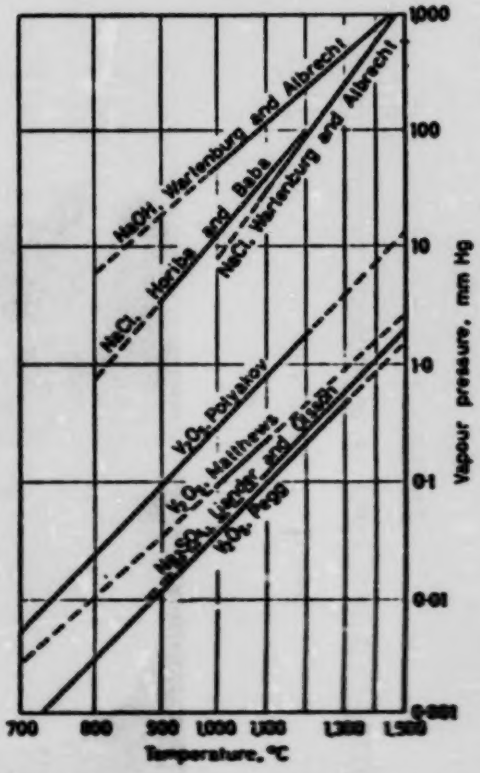


Fig. 5.4 Vapour pressures of fuel oil ash constituents

6. EXPERIMENTAL PROGRAM

6.1 Research Plan

This section discusses combustion facilities, the design of the experimental program, test methodology, analytical procedures used for evaluating vanadium collection efficiency of the EPA Method 5 and ER&E stack sampling trains. The general approach taken in this investigation consisted of three phases:

1. State-of-the-Art-Review: An initial literature review was made to assess stack sampling and analytical methodology for collecting and analyzing vanadium-containing particulate (both gaseous and solids) from fossil fuel combustion sources. The survey indicated that Atomic Absorption Spectroscopy followed by Arc Emission Spectroscopy are the two most precise and widely used techniques to analyze for vanadium-containing particulate (both gaseous and solids) from fossil fuel combustion sources. Collection of particulates in flue gas has been carried out with an ever-increasing number of devices. However, there is nothing in the literature to indicate that the standard fiber glass filter employed in the Method 5 sampling train is less efficient than other collectors. For particulate sizing, the Cascade Impactor, in spite of its many "stated problems", still remains the method employed by most investigators.

2. Develop Test Program: A factorial experimental program was developed and approved by the EPA. This program, conducted in our combustion facility, was designed to permit evaluation of vanadium particulate collection efficiency for a standard EPA Method 5 stack sampling train and an ER&E developed sampling system. It employs a factorial design to measure the interactions between several variables which were chosen because they might affect the amount of vanadium in the flue gas and the size distribution of the vanadium emissions. These variables were combustion chamber residence time and fuel composition (ash and asphaltene content). Two levels of residence time and three typical heavy fuel oil compositions were selected for evaluation. In addition, two sampling locations, 90° apart in the stack, were included as variables in the study to eliminate any bias attributable to particulate maldistribution in the flue gases. To evaluate these factors, 36 experiments were planned - 12 base runs, each with two levels of replications. An important aspect of the test procedure was the simultaneous operation of both sampling trains in each test. This feature not only served to double the data base, but it also eliminated sample bias attributable to run to run fluctuations in boiler performance. This influenced our decision to use restricted randomization for selecting the sequence of experiments.

The key to evaluating sampling system collection efficiency was a vanadium balance around the boiler. By knowing the vanadium content of the fuel which is burned and determining the amount of vanadium that deposits in the boiler, it is possible to establish how much vanadium enters the stack. The amount not accounted for in the sampling train represents the combination of collection inefficiency and/or experimental error in measurement and other inaccuracies.

To accomplish a vanadium material balance in the boiler, two methods were originally proposed. The method actually used in the study consisted of inserting a removable, thin wall, stainless steel liner into one heat exchanger tube in each boiler pass. At the end of a test, the inserts were removed, their contents were inventoried and assayed for vanadium. Assuming that the combustion gases were not maldistributed, the amount of vanadium found in one insert times the number of heat exchanger tubes in that particular pass equalled the amount of vanadium deposited. This method has two potential causes of inaccuracy. The first is the supposition that combustion gases flow equally through all the heat exchanger tubes. The other shortcoming results from not being able to inventory the two water backed face plates in which the heat exchanger tubes are set. These plates account for about 10% of the total surface area of the passes.

In order to overcome these problems, a second method was proposed involving isokinetic sampling of the combustion gases at the end of the firetube. The advantage of sampling there is that the combustion gases have not as yet gone through any heat exchanger tubes or return sections, which tend to collect particulates. Thus a material balance would obviously be facilitated.

The disadvantages of sampling in the firetube are that the gases are still very hot and that there may be greater maldistribution of particulates than in other sections. At the point where the sample would be taken, gas temperature is 1100-1600°F depending upon combustion conditions. The gas sample would have to be quenched rapidly from firetube temperature to 400°F in the collection system. Since some of the ash components might still be vaporized at firetube temperature, this quenching would cause them to precipitate in a different form than they might have in a heat exchanger. Thus size distribution might be affected.

Particulate maldistribution may come about from inhomogeneities in the flame and the swirl imparted to the combustion gases by the burner. This problem simply means that greater care would have to be taken in traversing to get a good sample of the overall particulate loading.

In view of budget limitations it was decied only one method should be used. Since the tube inserts appeared the most practicable means of measuring vanadium deposits in the boiler, they were chosen. During the initial phase of the program several preliminary experiments were conducted to debug this technique. Samples from these runs were also used to establish the analytical methodology for determining vanadium content of the particulate.

3. Conduct Test Program: Paired tests were conducted in the package boiler during each week of operation. Experimental pairings were based on alternating combustion chamber residence time. This technique was employed as a means of minimizing the effects of possible long term fluctuations in boiler performance. Of the 36 tests constituting the factorial program only one (Run 61) had to be terminated and the results eliminated because

of problems traced to boiler operation. The entire test program required 5 months to complete. Additionally several experiments were made to determine changes in oxidation state of vanadium compounds retained on a filter when subjected to the stack gas environment.

6.2 Combustion Test Facility

6.2.1 50 hp Cleaver Brooks Package Boiler

All combustion experiments were carried out in a 50 hp package boiler having a nominal firing rate of 2 lbs/min. (15.0 gph) of residual fuel oil. This boiler is a horizontal firetube type; by means of appropriate baffles and heat exchanger tubes, the combustion gases are forced to pass the length of the boiler four times before being emitted into the stack. A cut-a-way view of a typical C-B boiler showing the four pass construction is illustrated in Figure 6.1. In these tests, firing rates of 2 lbs/min. and 0.5 lbs/min. were used. This difference represents a four-fold change in combustion chamber residence time; the reciprocal of firing rate ($\frac{1}{Fr}$) is roughly proportional to residence time. To amplify even more the effect of residence time, in those runs using the low firing rate an added second refractory chamber was butted to the existing combustion chamber. This increased the overall combustion volume by about 66% and residence time by an additional 1.6 times. When not required, the added refractory was removed from the boiler. Firing rate and fuel consumption were accurately metered in each test by periodically monitoring the loss in weight of the oil supply drum. Atomization of the residual fuel oil was accomplished by maintaining a constant volume of air at low pressure (10 psi) on the burner gun. In all tests the fuel oil viscosity at the atomizing nozzle was maintained at 30 centistokes by heating the fuel to a predetermined temperature with an electrical heater.

Secondary air for combustion was furnished by a centrifugal blower mounted in the boiler head. The air was forced through a diffuser plate to thoroughly mix with the atomized oil before combustion. The amount of the secondary air was controlled by means of a damper which was regulated to keep oxygen concentration in the flue gas, normally at 2% (∿10% excess air).

For monitoring boiler performance, the concentration of CO, CO_2 and O_2 in the flue gas was continuously measured using Beckman instruments. Both carbon monoxide and carbon dioxide were measured using nondispersive infrared analysis while oxygen was determined polarographically.

Figure 6.2 is a front view photograph of the Cleaver Brooks boiler illustrating the oil supply drum monitoring arrangement and air control damper/burner housing. Figure 6.3 shows the instrument bank (foreground) for monitoring composition of flue gas. Controls for the stack sampling systems are positioned alongside the boiler.

To insure operational stability, the package boiler was allowed to warm up for a minimum of one hour before the start of a run which would normally last from 1-2 hours. During the test, minor adjustment of the secondary air to maintain flue gas oxygen concentration at 2% was normally the only control required to hold conditions constant. The oil firing rate was set immediately upon start up of the boiler. Temperature of the combustion gases at passes 1, 2 and 3 as well as in the stack were recorded continuously. Other ancillary measurements included pressures in

THE FOUR PASS CONSTRUCTION OF A TYPICAL C-B BOILER

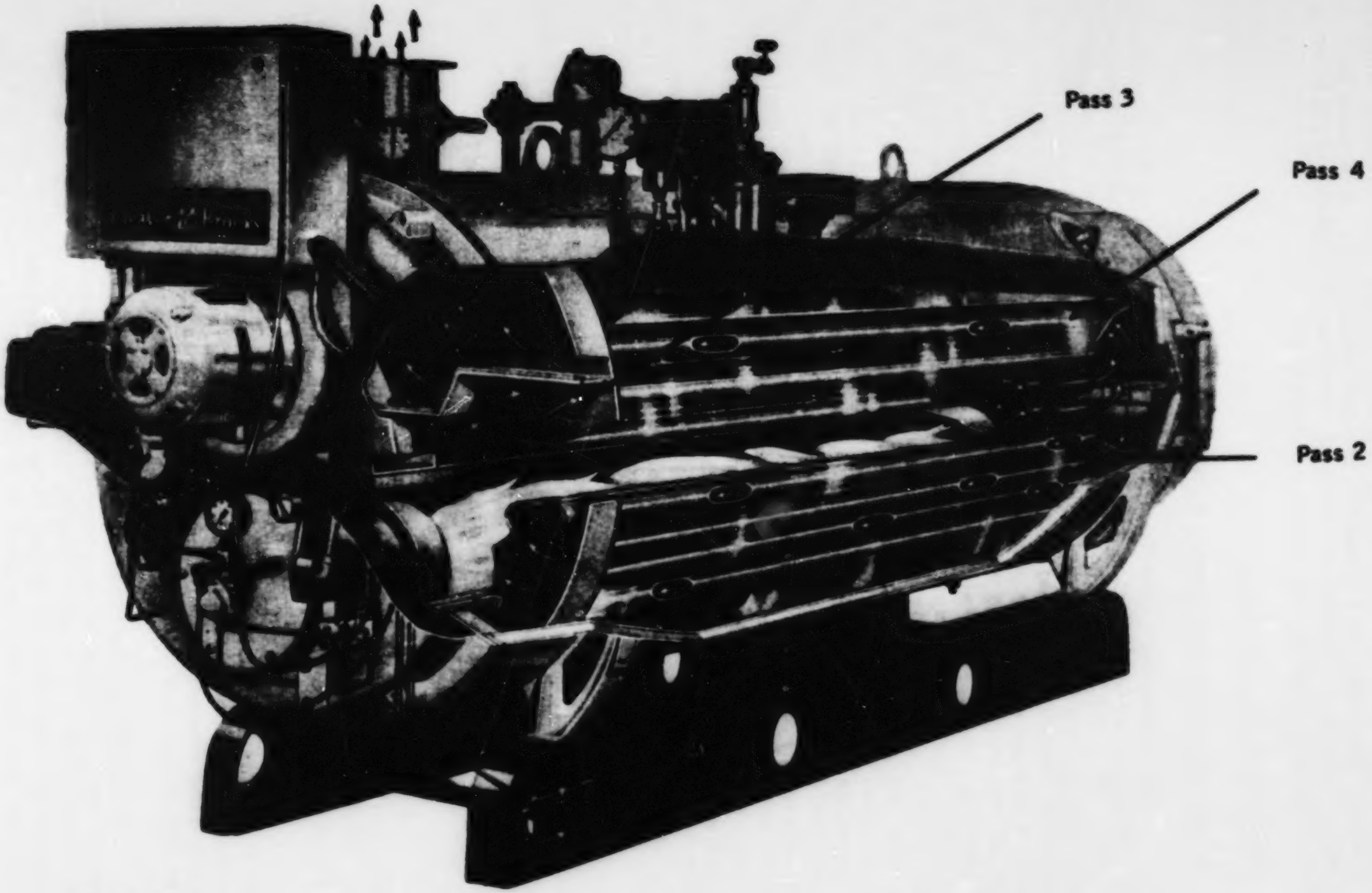


FIGURE 6.1

This cutaway view shows the gases are constrained to flow through the four passes in the order indicated. The combustion air enters the burner through an Adjustable Damper. The blower forces air through the diffusor and into the combustion chamber, this constitutes Pass (No. 1). Baffling allows gases to pass to the front of the boiler only through Pass (No. 2). A plate constrains gases to travel to the rear of the boiler through Pass (No. 3). From the rear head,gases are forced through Pass (No. 4) to the stack.

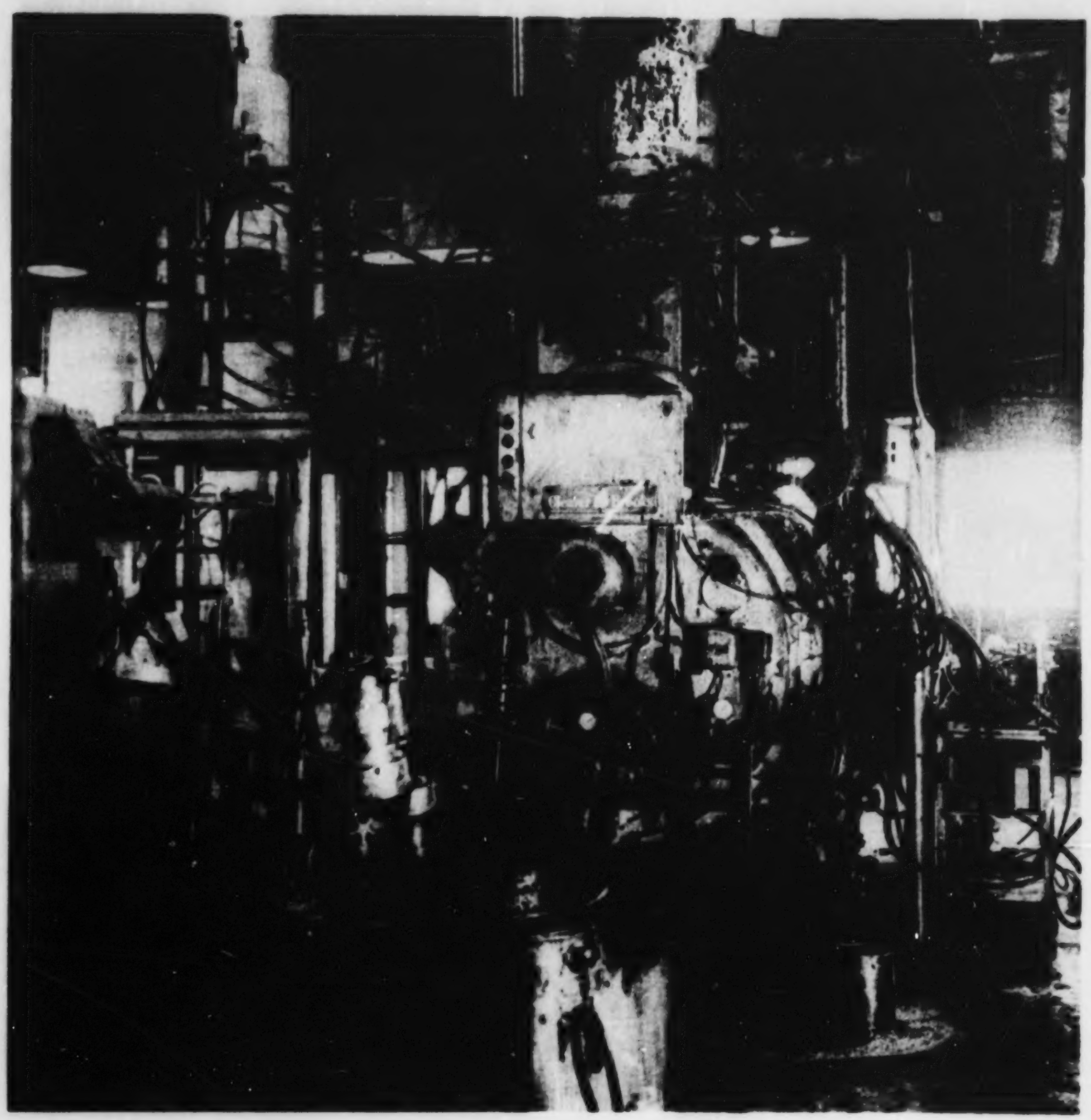


FIGURE 6.2 - 50 HP CLEAVER BROOKS BOILER

FRONT VIEW OF BOILER SHOWING OIL SUPPLY MONITORING SYSTEM, AIR DAMPER CONTROL AND BURNER HOUSING.

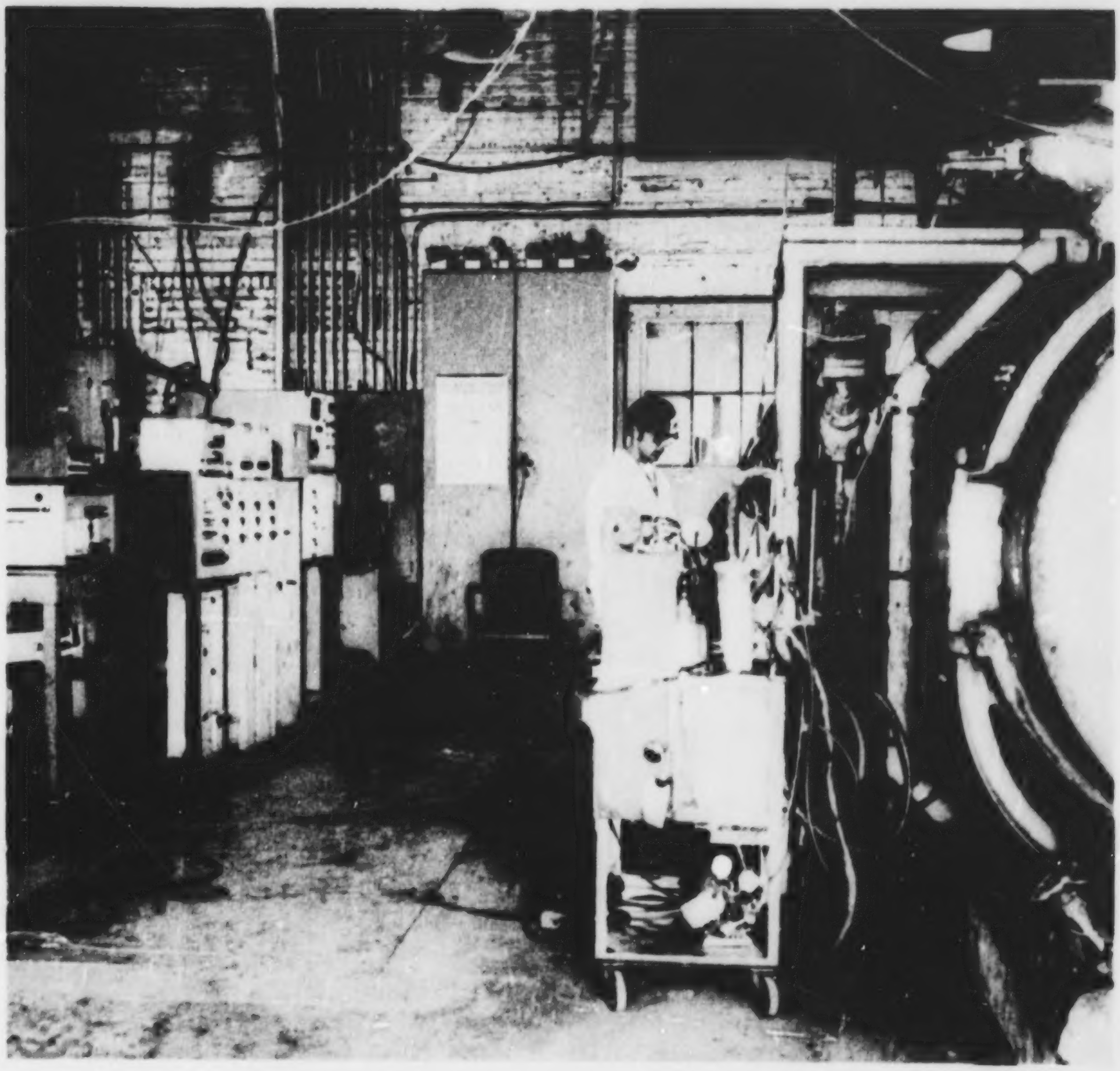


FIGURE 6.3 - ARRANGEMENT OF FLUE GAS MONITORING SYSTEMS

FOREGROUND: INSTRUMENTS INCLUDE CO, CO_2, O_2 AND NO_x MONITORS. CONTROL EQUIPMENT FOR PARTICULATE SAMPLING TRAINS IS POSITIONED NEAR BOILER.

the windbox and end of first pass, and back pressure on the oil line and atomizing air line.

6.3 Program Design

The object of our experimental program was to measure and compare the effectiveness of the standard EPA type stack sampling system and the Exxon Research developed system for collecting vanadium emissions from combustion of appropriate residual fuel oil. A standard EPA type train was used which consisted of an 18 inch glass lined probe, a cyclone, a glass fiber filter (125 mm, Type MSA-1106BH) and two chilled water impingers. With the exception of the latter all components were heated to 400°F. The ER&E system comprises an 18 inch glass lined probe, an 8-stage Andersen Cascade Impactor and two silicone oil-containing impingers, all heated to a temperature of 400°F. As back-up to this system, a dry ice-acetone finger trap at -100°F was used in the line after the last impinger to condense any volatile vanadium compounds.

The reliability of the two systems, i.e., the ability to collect all of the vanadium-bearing materials entering the stack sampling system was determined on the basis of a vanadium balance made around the boiler. Inventorying the particulate fallout in the four boiler passes was accomplished with removable, thin wall, stainless steel liners inserted in one of the heat exchanger tubes in each pass. At the end of a test the inserts were removed, their contents were collected and weighed by the same means used for isolating sample probe solids. Analysis for vanadium in the particulate was made using atomic absorption spectroscopy.

It was expected that particle size distribution of the vanadium particulate would have a major bearing both on the amount of material that deposits in the boiler tubes and on the collection efficiency of the stack sampling systems. Since the concentration and chemistry of vanadium in the fuel during combustion could influence this distribution, residual fuel oils encompassing a range of ash contents and asphaltenes (hexane insoluble material) were employed. Selected resids included a high and an intermediate sulfur fuel oil produced from Venezuelan (Tia Juna Medium) crude and a high sulfur Light Arab fuel oil. All fuels are typical of those currently being used in the United States. Key inspections are presented in Table 6.1. Complete analyses are shown in Table 6.2.

TABLE 6.1

Residual Fuel Oils Used in V Collection Efficiency Study

Fuel Designations & Type	Sulfur Wt. %	Vanadium wppm	Nickel wppm	Ash wt.%	Asphaltene Content (Hexane Insolubles) Wt. %
F_1, Hi. S (Venezuelan)	2.2	359	63	0.09	12
F_2, Med. S "	1.0	149	26	0.05	5
F_3, Hi. S. (Light Arab)	2.8	39	10	0.01	4

TABLE 6.2

Heavy Fuel Oil Inspections

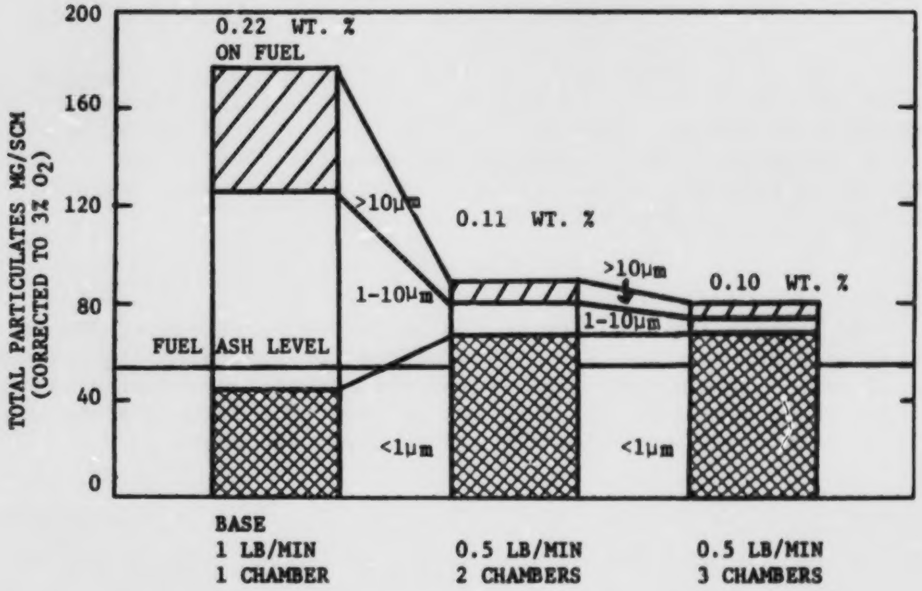
Inspection	Low Ash Light Arab Test Fuel F_3	High Ash Venezuelan Test Fuel F_1	Intermediate Ash Venezuelan Test Fuel F_2
% Ash	0.01	0.09	0.04
B S & W	0.06	0.16	0.80
BTU/#	18,708	18,540	18,976
% Carbon	85.22	84.73	86.63
% Hydrogen	11.04	11.23	12.24
% Sulfur	2.84	2.20	0.96
Con Carbon	7.18	12.70	5.63
Flash Point, °F	220	178	216
API Gravity, 60°F	16.4	14.7	20.7
% Hexane Insolubles	3.74	11.79	4.98
% Nitrogen	0.21	0.48	0.28
Pour Point	+40	+20	-10
Sed. by Hot Filtration	0.02	0.20	0.20
Vis. SSU @ 100	1444	4694	500
Total Oxygen %	0.20	0.42	0.40
Metals, ppm			
V (Range)	37-42	335-383	138-158
Na	Trace	24	10
Ni	10	63	26
Fe	10	9	6

Of the two Venezuelan fuel oils it may be noted that ash and asphaltene contents are roughly proportional to their sulfur content. This results from the desulfurization process used. Since ash and asphaltene in the Venezuelan residua cause intolerable catalyst deactivation in the desulfurization process, the residuum is vacuum distilled before it is hydrotreated. Only the overhead cuts from the vacuum tower, which are free of ash and asphaltenes, are desulfurized. A portion of the high sulfur vacuum bottoms is blended back into the desulfurized vacuum gas oil to make the final low S fuel oil. The amount which can be added is limited by the fuel oil S target. A 1% sulfur fuel oil contains only about half as much vacuum resid as the high sulfur (2%) fuel oil. Since all of the ash and asphaltenes are contained in the vacuum resid the concentrations of these components are proportional to the sulfur content. Thus a 1% S resid would have about half that of a 2% S fuel oil.

Residence time in the combustion zone is a major variable affecting particle size distribution and distribution of vanadium among the particle size range. Residence time is also one of the primary differences between different sized boilers. Previous studies at Exxon Research have measured the change in particulate distribution as a function of residence time. This effect is illustrated in Figure 6.4. As residence time in the combustion zone increases, more of the large carbonaceous particles are consumed, shifting size distribution toward submicron particles. These are generally the most difficult to collect in a sampling system. A major change in size distribution resulted from cutting firing rate in half with an extra combustion chamber. Total particulates decreased by about half to 0.11 wt.% and almost all the cenosphere and intermediate size particles were consumed. Inorganics and refractory carbon material comprised the remaining particulate.

FIGURE 6.4

LONGER RESIDENCE TIME FAVORS BURNOUT OF CENOSPHERES



In the experimental program, two levels of residence time were studied. For the base level (τ_0) tests were run at a firing rate of 2 lbs/min. (15 gal/hr.) using the normal combustion chamber configuration. At this combustion condition the calculated volumetric flow rate was on the order of 450 cu. ft./min., which gave a residence time of roughly 50 msec in the combustion chamber. In this case large particulate dominated the size distribution. For the second level (τ_1), firing rate was decreased to 0.5 lbs/min. (3.5 gal/hr.) and an additional refractory chamber was added. These changes produced about a 7-fold increase in residence time to 350 msec. More importantly, at this combustion condition carbonaceous material burned off and the particle size distribution was shifted toward the submicron range.

As both residence time and fuel composition are main variables which may influence vanadium collection efficiency a factorially designed experimental program was employed. The program plan is outlined in Table 6.3. There were 12 different experiments each replicated three times for a total of 36 runs. As previously indicated both EPA and ER&E sampling trains were operated simultaneously in each experiment. This was possible by using two ports located at right angles to each other in the boiler stack. To prevent the possibility of sample bias, since it was not feasible to make a standard traverse in each port for every run, the sampling train positions were rotated as indicated in the table. On the basis of finding no statistical difference between results from the two positions, the experimental design allows the pooling of these data. In essence, this would double the number of replications and degrees of freedom in defining the experimental error.

Selection of the order in which the experiments were run was based on a restricted randomization. With truly randomized tests, there is a finite probability that a block of experiments involving a particular residence time (τ_0 or τ_1) will be grouped toward either end of the program. Any long term change in boiler performance would influence residence time and seriously prejudice the results. Since we were interested in comparing collection efficiency of the sampling systems for vanadium particulate emitted in different size ranges, a restricted test approach was used. Accordingly, paired tests, a test at one residence time followed by the same test but at the other residence time were used. Since only two tests a week could be run, this grouping was most efficient.

To analyze for vanadium in the collected particulate, Atomic Absorption spectroscopy was used. This method combines both high precision with rapid sample throughput. The latter means that many samples can be run in a short time period. This was an important feature since over the life of this study approximately 475 samples were analyzed.

TABLE 6.3

Experimental Program Design

	Stack Sampling Probe Location (1) EPA ⟶ | EPA Vs. ER&E			Stack Sampling Probe Location (2) ER&E Vs. EPA | ⟵ EPA			
	Residual Fuel Type			Residual Fuel Type			
	F_1 Hi S Ven.	F_2 Med S Ven.	F_3 Light Arab	F_1 Hi S Ven.	F_2 Med S Ven.	F_3 Light Arab	
	Run No.	Run No.	Run No.	Run No.	Run No.	Run No.	
Residence Time	55	48	47	52	45	50	Cycle 1
τ_0 = 50 msec.	57	69	61*	71	63	58	Cycle 2
Standard - Normal Combustion Chamber, 15 Gals/hr. firing rate	68	75	78	79	74	65	Cycle 3
Residence Time	54	49	46	53	44 (start)	51	Cycle 1
τ_1 = 350 msec.	56	70	60	72	62	59	Cycle 2
~7 fold increase with double chamber and 3.75 Gals/hr. firing rate	67	76	77	80 (finish)	73	66	Cycle 3

- Experimental order based on restricted randomization of pairs.
- Total experiments = 36
- Time frame = 5 months

Notes on Experiments

*Run No. 61 was terminated after boiler upset. No data obtained in this run.

6.4 Boiler Tube Inserts

Each of the passes in the Cleaver Brooks boiler consisted of cooled heat exchanger tubes, 121 inches long by 2-1/4 inches internal diameter. There are fourteen of these tubes in pass 2, ten in pass 3 and eight in pass 4 providing a total of 192 ft.^{2} of heat exchanger surface area. Pass 1 is significantly different from the others. It consists of a refractory lined combustion chamber 30 inches long x 12 inches diameter expanding into a water backed firetube, 19 inches in diameter. As summarized in Table 6.4, the firetube (pass 1) accounts for roughly 15% of the total heat exchanger surface area. Pass 2 has the greatest surface area, accounting for 33%. Pass 3 accounts for 24%, while pass 4 makes up 19% of the area. There are water backed face plates at either end of the boiler which could not be inventoried for vanadium particulate. These account for 9% of the surface area.

TABLE 6.4

Heat Exchange Surface in the Cleaver Brooks

Pass	No. of Tubes	Total Surface Area, Ft.^{2}	% of Total
1	(firetube)	37.6	15
2	14	84.0	33
3	10	60.0	24
4	8	48.0	19
Ends		22.0	9
		251.6	100

Particulates are thought to deposit within the heat exchanger section by two mechanisms. Large particles drop out by impaction on the walls of the tube or in the headers where gases reverse direction between passes. It was not possible to collect and inventory particulates from the headers after each run so this is a potential source of error.

The other collection mechanism is thermal or molecular diffusion of fine particles to the walls of the tubes. The temperature gradient between flue gas and water backed metal surface served as a driving force for diffusion. Since metal surface was essentially constant,this varied from pass to pass and between runs. Table 6.5 shows temperature levels measured in each pass at high and low firing rates. By the end of the second pass, temperature has dropped to within a few hundred degrees of stack temperature, especially at low firing rate. Thus driving force for thermal diffusion is highest in the first two passes.

TABLE 6.5

Influence of Combustion Conditions on Boiler and Stack Temperatures

Temperature °F	Fuel Firing Rate, lbs./min. 0.5	Fuel Firing Rate, lbs./min. 2.0
End Pass 1	1060	1625
End Pass 2	380	705
End Pass 3	283	500
End Pass 4	225	360
Stack	220	355

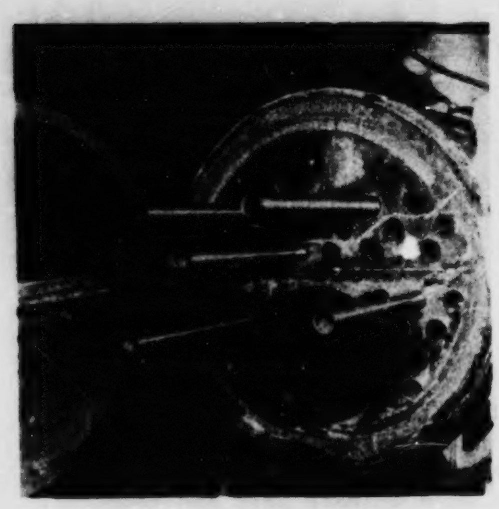
Removable thin wall stainless steel liners were used to measure particulate and vanadium fallout in the passes. These were machined from 304 seamless 2-1/4 inch OD x .065 wall OD pipe. These liners were inserted during a run into one tube in each pass and then removed and their contents inventoried at the end of each run. Since it was not possible to sample the firetube by this method, a manual cleaning method was used, (sweeping out the firetube). In Figure 6.5, photographs A and B show the back end of the Cleaver Brooks boiler with removable liners inserted in the various passes. The pictures show two tubes per pass, but in most runs only one per pass was used. The 14 second pass tubes are around the firetube in the bottom half of the boiler. The chalk line drawn across the boiler facing separates the 10 tubes in the third pass from the 8 tubes in the fourth pass. Combustion gas enters the third pass at the front end of the boiler. Since this area is not easily accessible, a locking collar was welded into three of the tubes to prevent channeling of the gas stream between liner and tube. Channeling was prevented at the back end of the boiler by a collar welded on the liners. The collar fits tight against the tube and face plate providing a seal. Photographs C and D show the firetube ,refractory lined combustion chamber and a front view where the burner housing has been exposed.

6.5 Stack Sampling Systems

6.5.1 EPA Method 5

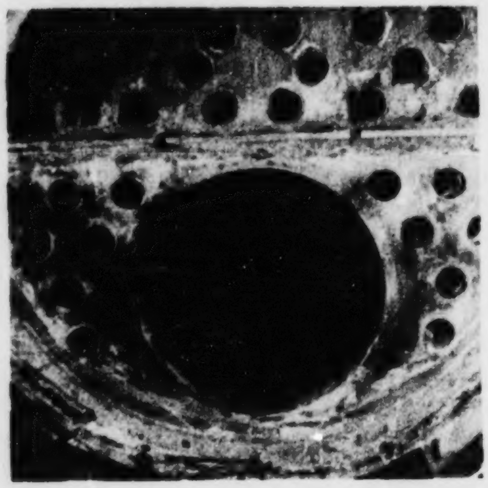
The EPA Method 5 stack sampling system used in this study was a commercially available Joy Emission Parameter Analyzer. This unit consisted of an 18 inch glass lined probe, a cyclone, a 125 mm glass fiber filter (filter type MSA-1106BH) and two water impingers. The configuration is shown schematically in Figure 6.6. With the exception of the impingers, the entire sampling train was maintained at 400°F in every run. This insured that stack gases entering the sampling system were well above the acid dew point. Therefore sulfuric acid could not condense on the collected particulate or the walls of the equipment.

FIGURE 6.5 - FOUR PASSES OF CLEAVER BROOKS BOILER

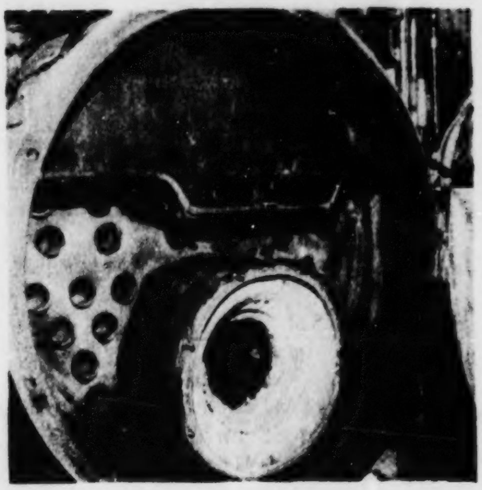


A. THIN WALL STAINLESS STEEL REMOVABLE LINERS FITTED INTO SELECTED HEAT EXCHANGER TUBES IN PASSES 2, 3 AND 4. (BACK END VIEW) - COLLAR ON END OF LINER PREVENTS CHANNELING OF THE COMBUSTION PRODUCT GAS STREAM.

B. BACK TO FRONT VIEW OF BOILER ILLUSTRATING CENTRAL FIRETUBE AND HEAT EXCHANGER TUBES. REMOVABLE LINERS HAVE BEEN INSERTED INTO HEAT EXCHANGER TUBES. CHALK MARK OUT LINE INDICATES TUBES IN PASS 3 AND 4.



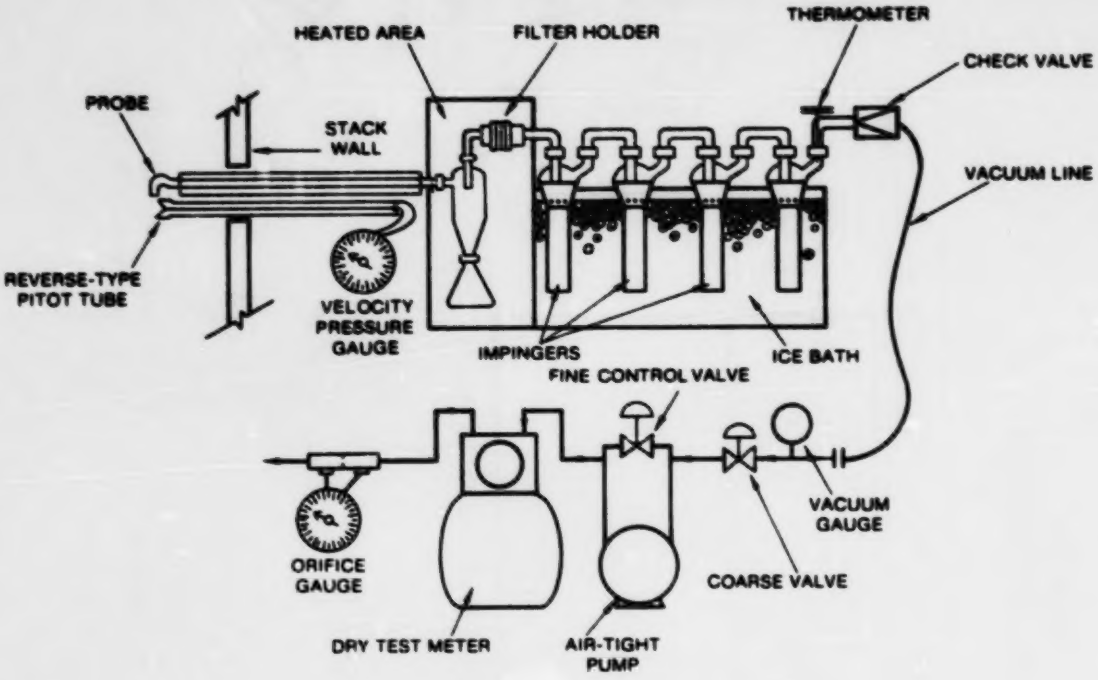
C. CENTRAL FIRETUBE LOOKING TOWARD BURNER GUN. AREA OF REFRACTORY LINING IS THE COMBUSTION CHAMBER.



D. FRONT VIEW OF BOILER WITH BURNER HOUSING AND ACCESS DOOR REMOVED. SHELF SEPARATES PASS 4 FROM PASS 3.

FIGURE 6.6

EPA Method 5 Sampling Train


HEATED AREA
FILTER HOLDER
THERMOMETER
CHECK VALVE
PROBE
STACK WALL
VACUUM LINE
REVERSE-TYPE PITOT TUBE
VELOCITY PRESSURE GAUGE
IMPINGERS
ICE BATH
FINE CONTROL VALVE
VACUUM GAUGE
ORIFICE GAUGE
COARSE VALVE
DRY TEST METER
AIR-TIGHT PUMP

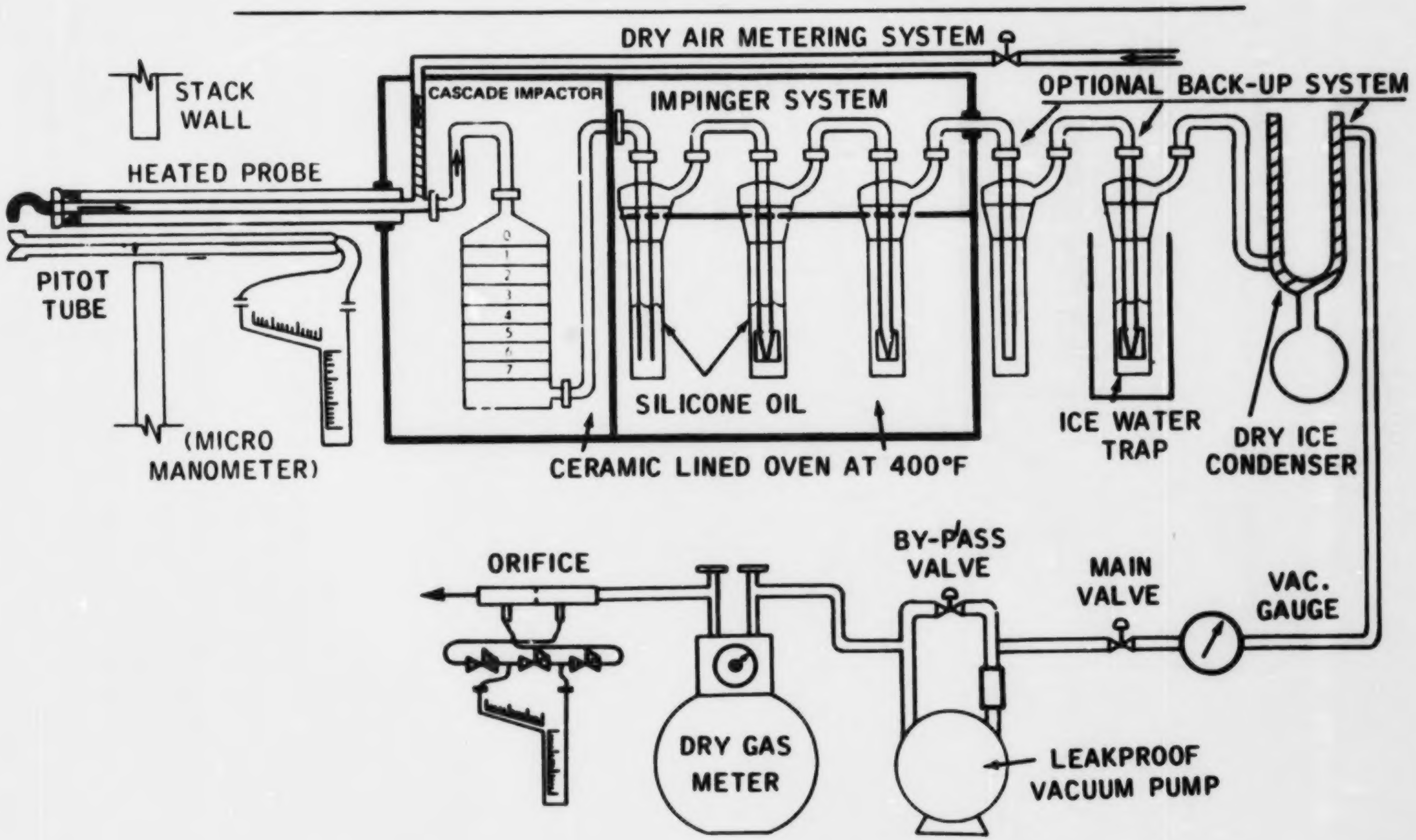
6.5.2 ER&E Collection System

Because of the problems with existing stack sampling trains and to meet the Company's program needs, ER&E developed a system several years ago with more analytical capability than Method 5. This system permitted segregation of particulate into several size fractions; it eliminated the formation of "artificial type particulate" and it allowed collection of relatively large samples which could be quantitatively recovered for analysis. Rather than spend considerable time and effort in hardware development, the best available components were selected and built into a sampling system. Thus the stack sampling train illustrated in Figure 6.7 evolved.

The heart of the system is an Andersen eight stage Cascade Impactor and several Greenberg-Smith, high velocity impingers filled with silicone oil. These are all mounted in an oven maintained at 400°F. The high temperature impingers make it possible to obtain a true inventory of "real particulate" with no sulfuric acid formation or hydrocarbon condensation. Both can and do occur in cold water impingers to a different degree than they do in stack plumes. Since particulate loading is reported on a mass basis, a more accurate inventory is possible with the ER&E system

FIGURE 6.7

ER&E STACK SAMPLING TRAIN


DRY AIR METERING SYSTEM
STACK WALL
HEATED PROBE
CASCADE IMPACTOR
0
1
2
3
4
5
6
7
IMPINGER SYSTEM
OPTIONAL BACK-UP SYSTEM
PITOT TUBE
(MICRO MANOMETER)
SILICONE OIL
ICE WATER TRAP
DRY ICE CONDENSER
CERAMIC LINED OVEN AT 400°F
ORIFICE
BY-PASS VALVE
MAIN VALVE
VAC. GAUGE
DRY GAS METER
LEAKPROOF VACUUM PUMP

In most of the experiments, a sampling rate of about 0.90 SCFM was used with this system. With the isokinetic sampling requirement, however, when that amount of flue gas could not be withdrawn, dry filtered makeup air was provided to the unit upstream of the cascade impactor. With this provision, it was possible to still sample isokinetically while maintaining a fixed flow rate through the impactor and impingers. The makeup air was heated to 400°F and supplied at atmospheric pressure. To alleviate the problem of wall loss and particle bounce in the cascade impactor, it was found necessary to have leak-proof operation and during sampling maintain a constant volumetric flow rate through the system.

Particle distribution was divided into three (mass) size ranges: >10 µm, 1-10 µm and 1 µm. The amount in each of these ranges was determined mathematically by plotting on logarithmic probability paper the aerodynamic particle diameter versus cumulative weight percent of the collected particulate. Aerodynamic diameter was determined based on a computer solution of the Ranz-Wong equation(20) for the individual stages of the Andersen Impactor. The 50% cut-off points (D_{50}) calculated for the stages were generally in agreement with the manufacturer's values. At the conditions employed, stage 0 had a cut-off of approximately 10 µm while stage 5 had a cut-off of roughly 1 µm. On this basis, all material isolated from stages 6 and 7 plus the impingers made up the submicron particulate fraction.

As further illustrated in Figure 6.7, the ER&E system uses a dry ice-acetone cold trap at -100°F to insure knock-out of any volatile compounds. The two impingers outside the oven section, one empty and the other containing chilled water, remove silicone oil or other materials entrained by the flue gas. The probe was designed to obtain even heating over its entire length. To minimize particle deposition the probe length was kept to a minimum, about 18 inches.

Figures 6.8 - 6.12 are photographs of the EPA and ER&E sampling trains and major components making up the ER&E system. Figure 6.9 and 6.10 illustrate the arrangement used for sampling simultaneously with the two trains at the ports located 90° apart in the stack. This arrangement was designated in the factorial program as location 1. Location 2 was obtained by rotating the position of the sampling trains.

6.6 Particulate Sampling

Sampling of flue gas from combustion of heavy fuel oil in the Cleaver Brooks Boiler was carried out in a 12 inch circular stack. A single sample point located midway on the radius was employed for sampling particulate. This procedure was experimentally justified by our previous findings of uniform gas flow and particulate dispersion across the stack. Velocity profiles across the stack were determined with a standard 6-point pitot tube traverse (in the north-south direction). The traverse points were located at the center of each of

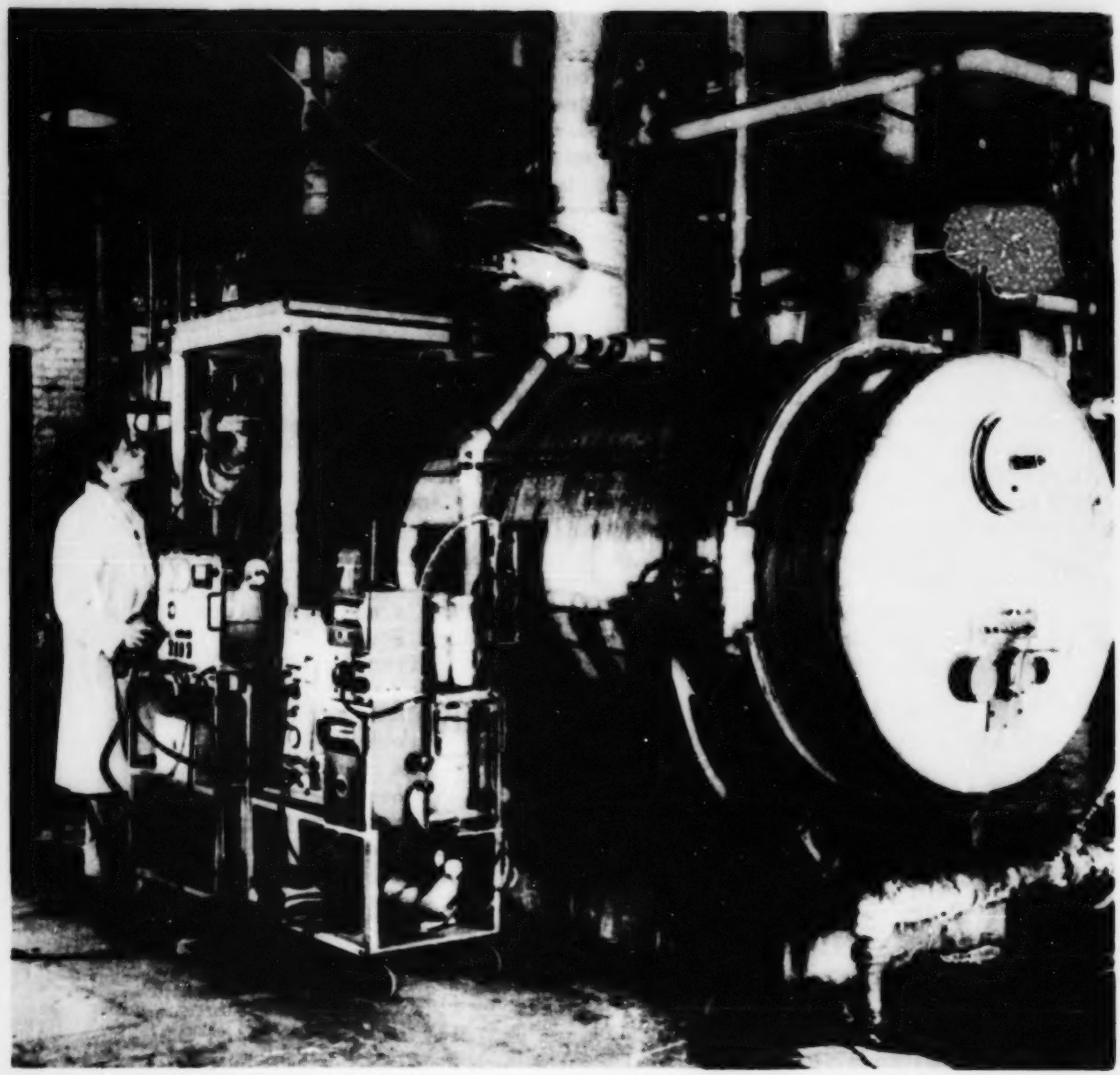


FIGURE 6.8 - OVERALL VIEW OF BOILER, STACK SAMPLING SYSTEMS AND CONTROL MODULES.

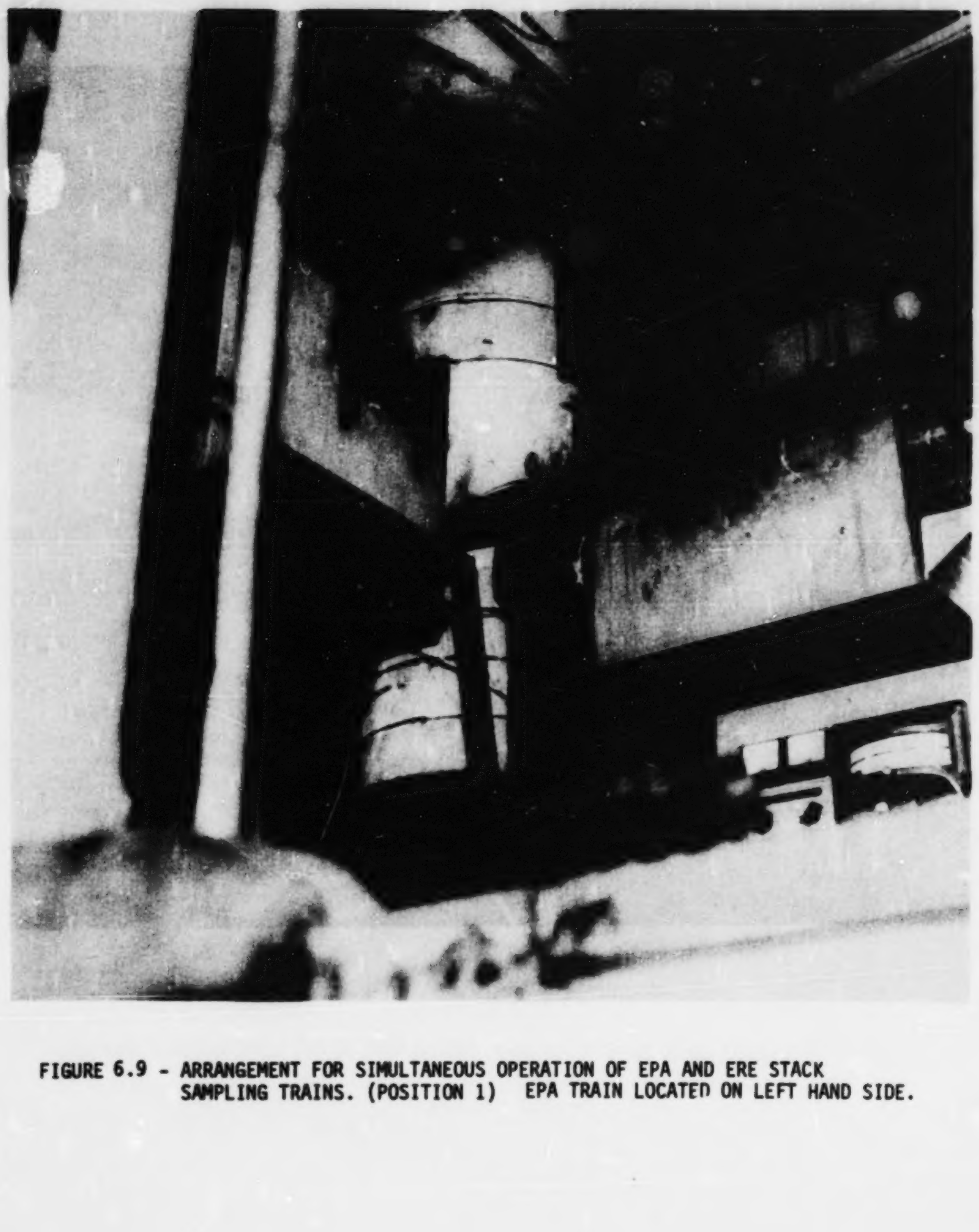


FIGURE 6.9 - ARRANGEMENT FOR SIMULTANEOUS OPERATION OF EPA AND ERE STACK SAMPLING TRAINS. (POSITION 1) EPA TRAIN LOCATED ON LEFT HAND SIDE.

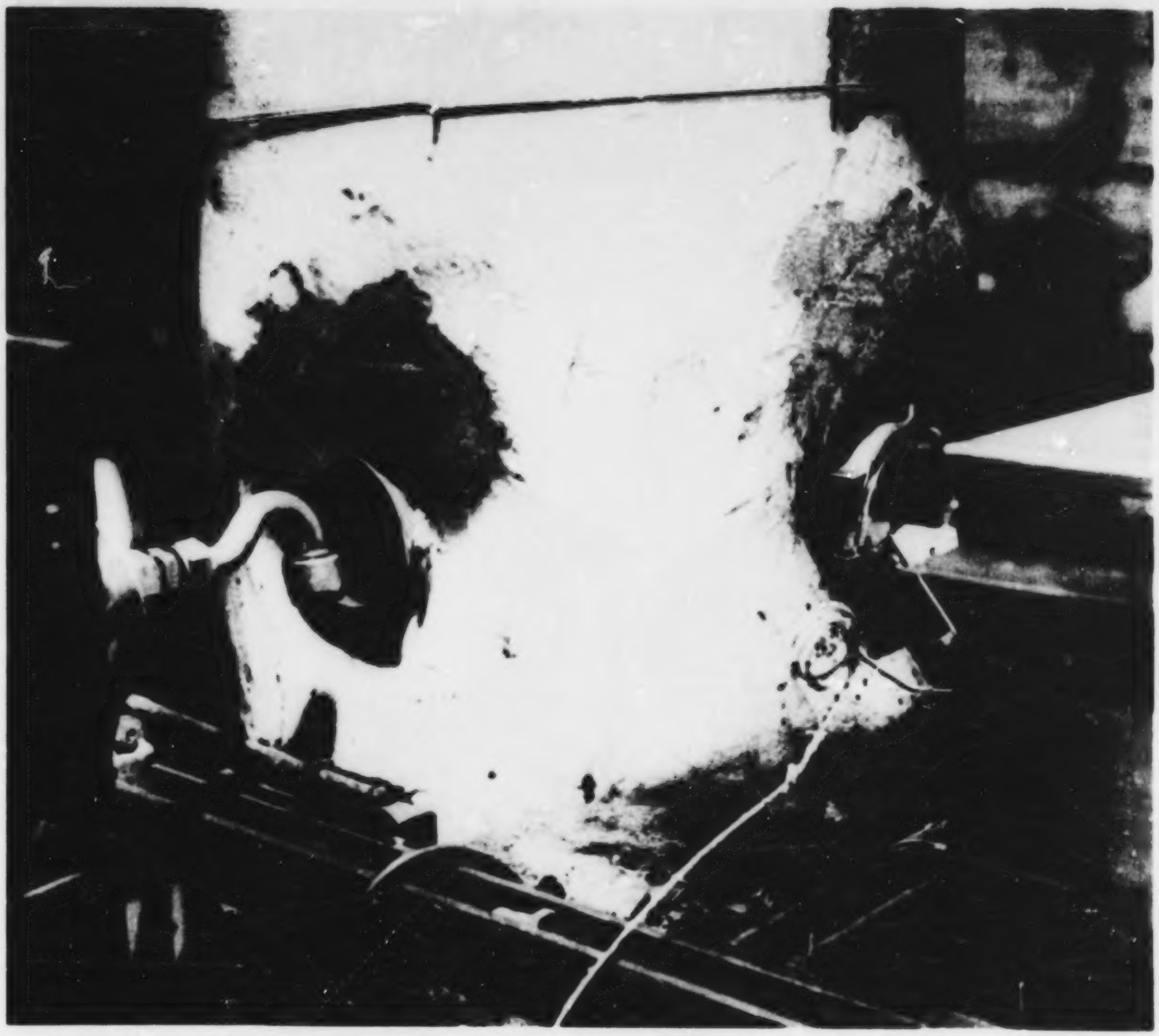


FIGURE 6.10 - CLOSE-UP VIEW OF PORT HOLE CONFIGURATION FOR SIMULTANEOUS SAMPLING.

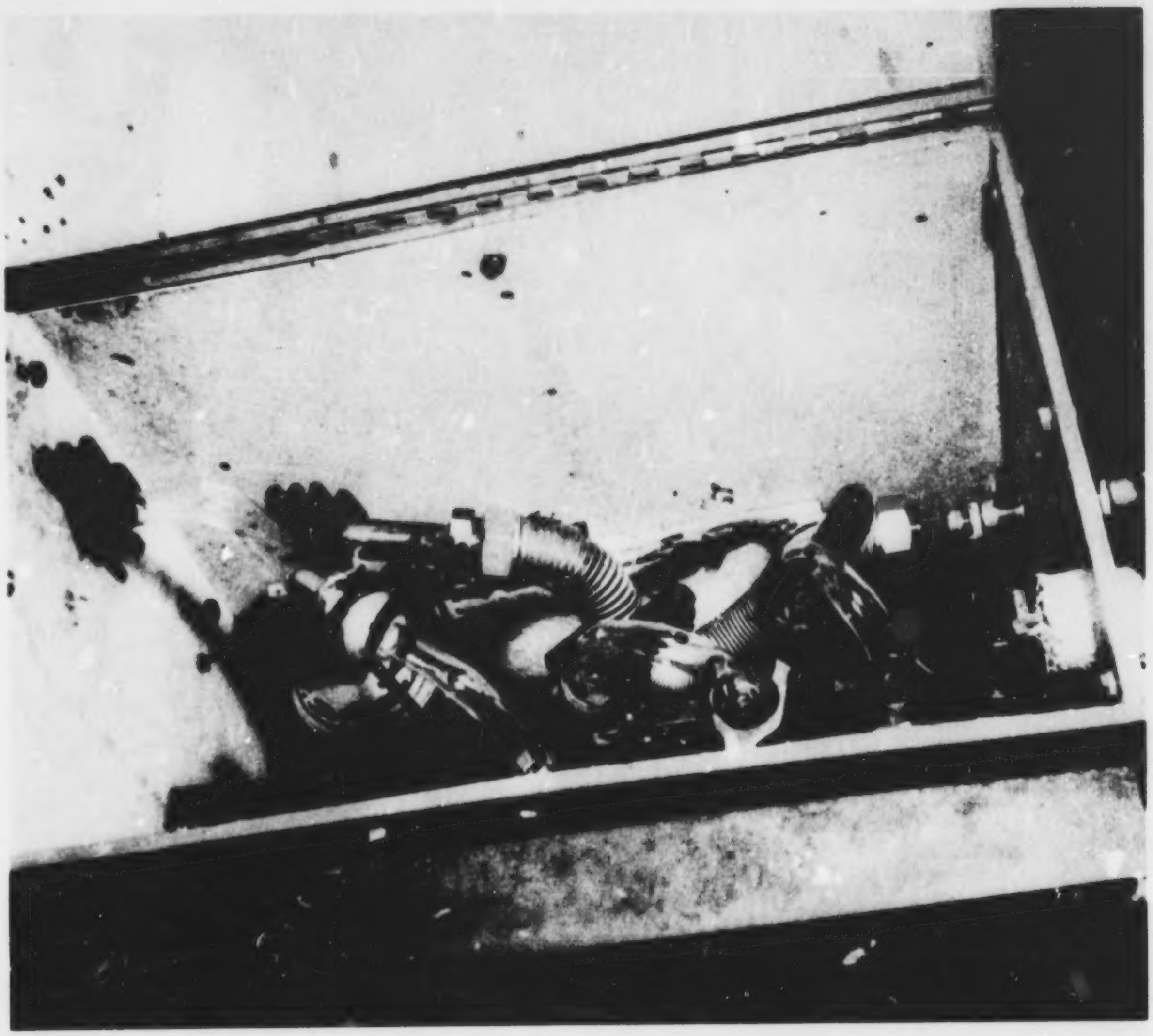


FIGURE 6.11 - OVEN ASSEMBLY OF ER&E SYSTEM SHOWING ANDERSEN CASCADE IMPACTOR, IMPINGER SYSTEM AND MAKEUP AIR LINE. GLASS TUBE UPSTREAM OF IMPACTOR IS CONNECTED TO PROBE.

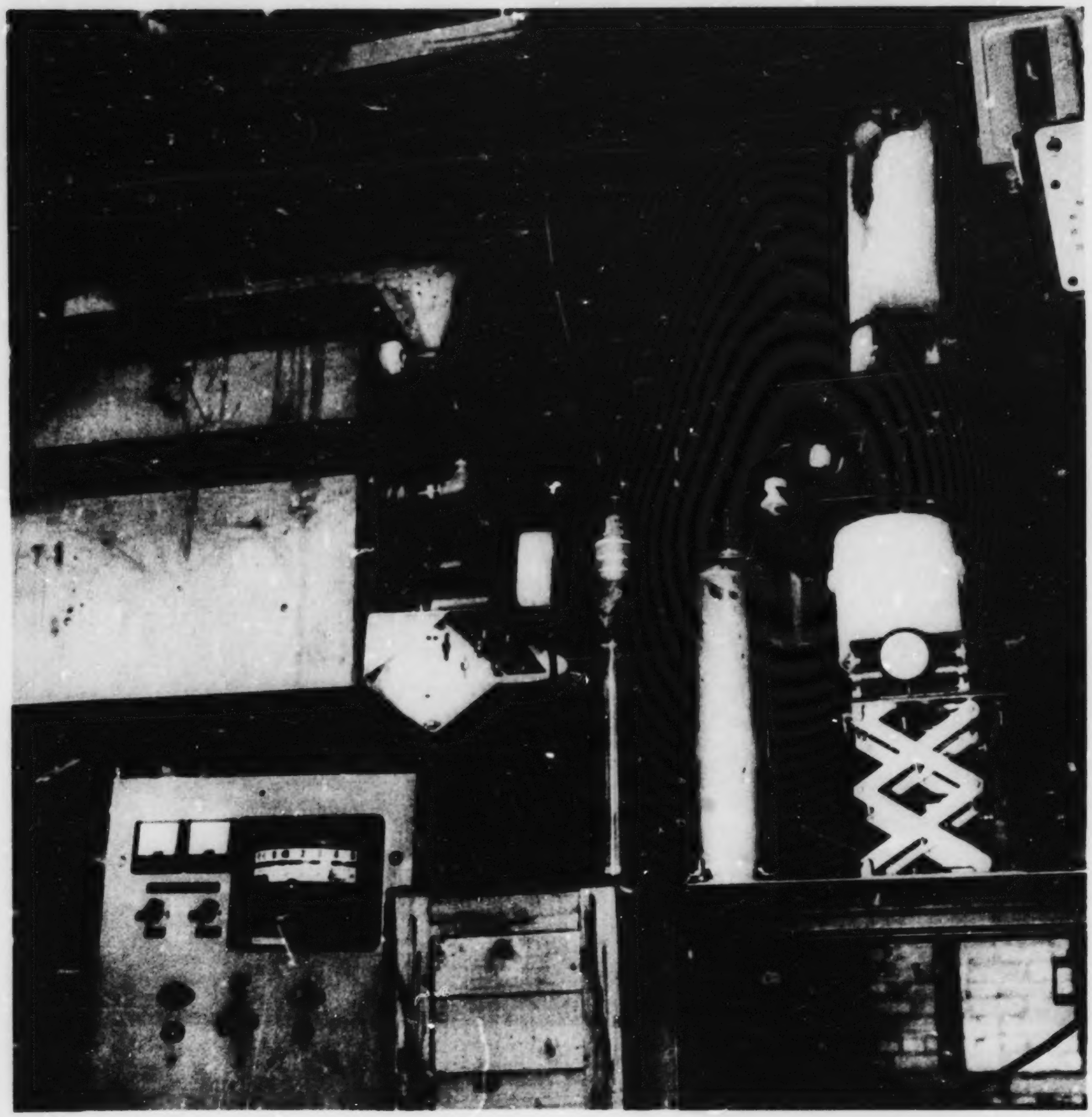


FIGURE 6.12 - VOLATILES KNOCKOUT SYSTEM CONNECTED TO ER&E TRAIN FEATURES A DRY ICE ACETONE COOLED CONDENSER.

six equal area zones. Representative results are illustrated in Table 6.6. Normally test conditions (firing rate and excess combustion air) are such that gas velocities on the order of a few feet/second are obtained. Hence calculated, flue gas velocity based on combustion conditions, is used for setting the isokinetic sampling rate. The agreement between calculated and measured values is quite good. The data in Table 6.6 also show the uniform flow behavior of the flue gas in the stack.

TABLE 6.6

Stack Velocity Profile from Boiler
(Fuel firing rate, 1.1 lbs./min. 10% excess air)

Traverse Point Number	(N/S) Distance into Flue Inches	Pitot Tube ΔP Inches H_2O	Stack Temp. °R	Stack Velocity, ft./min. Measured	Stack Velocity, ft./min. Calculated
1	0.5	0.011	680	401	368
2	1.8	0.011	700	407	379
3	3.5	0.010	740	399	401
4	8.5	0.010	752	402	407
5	10.2	0.011	750	421	406
6	11.5	0.011	748	420	405
Midpoint	6.0	0.010	743	400	402

A second port drilled into the stack at the same height but 90° removed (east-west direction) permits simultaneous withdrawal of particulate. Characteristic velocity profiles were developed for both sampling planes and are tabulated in Table 6.7. The data indicate a balanced flow across the stack. At the midpoint location,measured velocities were within 10% of each other and of the calculated velocity. Pitot tube readings (ΔP) were measured with an inclined Dwyer micromanometer.

TABLE 6.7

Low Level Source Profile
(Fuel firing rate $\sim$0.65 lbs/min)

Traverse Point Number	Distance Into Flue Inches	Pitot Tube ΔP Inches, H_2O	Stack Temp. °R	Stack Velocity, ft/min.	
				Measured	Calculated
N/S					
1	0.5	0.004	706	249	265
2	1.8	0.005	712	279	267
3	3.5	0.004	712	250	267
4	8.5	0.005	736	284	276
5	10.2	0.005	736	284	276
6	11.5	0.008	742	360	278
Midpoint	6.0	0.005	738	298	277
E/W					
1	0.5	0.005	730	283	274
2	1.8	0.005	728	282	273
3	3.5	0.005	732	283	275
4	8.5	0.006	734	310	275
5	10.2	0.005	738	283	277
6	11.5	0.008	744	361	279
Midpoint	6.0	0.005	734	283	275

In order to insure that the particulate mass flow rate was uniform from point to point within the cross section of the stack a similar type 6-point traverse was also made. The results are summarized in Table 6.8 and compared with the particulate catch obtained by simply sampling only at the midpoint in the stack. Both tests were conducted with marine bunker fuel. On average the mass concentration of particulates determined by the two procedures differed by only a negligible amount, about 1%. Comparing size distribution, however, only the mass concentration of submicron particulates was in agreement. The intermediate and large size fractions obtained by traversing the stack were almost the reverse of the distribution from single point sampling. Normally an 18 inch long sample probe is used to withdraw the flue gas. To accomplish the traverse, however, a 5 foot probe was employed. With the latter length there was considerable deposition of solids on the wall of probe. Although both large and intermediate size particles were probably present, the probe sample (by convention) was considered to be large particulate. This would, of course, bias the results in the direction observed in the table. Any decrease in the amount of solids attributed to the >10 µm fraction would produce an equivalent weight increase in the 1-10 µm fraction and, overall, would place the total particulate distribution in better agreement with the single point sample.

TABLE 6.8

Mass Concentration Profile in Stack is Uniform

Particulate Spectrum mg/SCM	I 6-Point Traverse (5 ft. probe)	II Single Point Sample (18 in. probe)
>10 microns	76.07	46.18
1-10 microns	50.72	92.37
<1 micron	126.78	118.03
- Total Mass	253.57	256.58
%Δ	—	1.2
- Wt. % on Fuel	0.32	0.32

Since both the total mass concentration of solids, and gas velocity, in the stack were steady (no variation with time) and uniform (no variation from point to point within the cross section) only one measurement is required for accurate results (21). While this measurement may be taken from anywhere within the cross section, a midpoint sample station has been utilized. It should be noted that even with an unsteady but uniform source condition, measurements are needed at only one location. In the later case, however, the measurements must be taken over an entire cycle, or over as long a time period as possible, for noncyclic operation. Although the Cleaver Brooks operation is indeed noncyclic a sampling time of up to three hours was used in the program.

6.7 Particulate Isolation Method - General Procedure

Recovery of particulate from the stainless steel liners inserted into the heat exchanger tubes of the boiler was accomplished using the same procedure employed for collecting the sampling probe solids. A water/organic solvent wash was normally all that was required to remove the solids quantitatively. In several experiments, an acid rinse of the tubes was employed as a back-up wash. Subsequent analysis for vanadium in the acid showed only trace quantities. Particulate from the firetube and the three other passes were kept segregated and analyzed for vanadium content separately. Prior to analysis each sample was dried under vacuum for a minimum of 4 hours, at a temperature between 250 and 300°F. Analysis of all particulate samples was carried out by Atomic Absorption Spectroscopy. The detailed procedure is presented in Appendix 3.

Isolation of the solids in both sampling trains were accomplished using the following general scheme:

Particulate matter from the various parts of the sampling train were isolated separately in order to determine net particulate weight. This was accomplished with water and organic solvent washings. Solvents were removed by evaporation and all particulate material was dried under vacuum at 300°F prior to weighing. The isolated solids were combined into three fractions for chemical analysis (normally only vanadium) and characterization. In the ER&E train these consisted of probe material and stage 0 of the impactor; stages 1-5 of the impactor; stages 6,7 and the impingers. For the EPA Method 5 train they consisted of probe and cyclone; filter, and impingers.

The detailed procedures used for isolation and characterization of the particulate are presented in Appendix 2.

6.8 Determination of Vanadium in Particulate

Atomic Absorption was the primary instrumental method used to determine vanadium content of the particulate in this study. It has high precision and it is fast. However it does require that the vanadium be in solution. To accomplish this, two procedures were initially evaluated.

In the first method, a series of particulate samples held in porcelain crucibles were ashed at 1450°F overnight. (This is a modification of the standard method of test for ash from petroleum product; ASTMD-482). While there was some concern that at this temperature V_2O_5 would volatilize, there has been no evidence to support this. On the contrary Foster et al(22), in a study of phase equilibrium.

relationships in the system $Na_2O-SO_3-V_2O_5$ found that a crucible containing V_2O_5 showed absolutely no weight loss in six hours at ∿1600°F. An identical test showed that a mixture of 20% Na_2SO_4 - 80% V_2O_5 lost no weight during 27 hours of exposure at 1600°F. It was further demonstrated by Milan (23) that in vacuo V_2O_5 begins to dissociate into V_2O_4 and O_2 at temperatures only slightly above its melting point of 1274°F. For example, at 1382°F the oxygen partial pressure in the gas phase corresponded to a melt containing 0.56% V_2O_5 while at 1832°F the melt contained 2.75% V_2O_4. It was also noted that the dissociation was reversible provided that the composition of the melt or condensed phase remained constant.

While V_2O_5 may not volatilize during the high temperature ashing, it does melt and fuse on the interior surfaces of the crucible. The melt also exhibits a tendency to creep up the side walls increasing the possibility for direct material loss. Dissolving the fused vanadium is extremely difficult and time consuming and there is no real assurance that all of the metal will go into solution. To avoid these complications, a second treatment labeled "liquid fire" was also evaluated. In brief, this method employs a digestion of the particulate sample using a mixture of concentrated acids, HNO_3, $HClO_4$ and H_2SO_4. In Table 6.9 vanadium analyses run by Atomic Absorption are compared for the two different ashing procedures. Samples of boiler deposits were obtained from several preliminary experiments (runs 33 and 34) made to check the reproducibility of the heat exchanger tube inserts. The deposits from the four passes in run 34 were ashed using both methods. In run 33 only the samples from passes 3 and 4 were tested in this manner, the other two were run using only the liquid fire method.

The results indicate a significantly lower vanadium content from the high temperature ashing procedure. Of the 6 samples run using both methods, only one showed agreement (9.3% vs. 9.2%), two other samples were about 10% apart. Where similar samples were subjected to high temperature ashing, the results also showed considerable variation in vanadium content. For the liquid fire treatment, samples from the two test series generally were in good agreement. As noted previously, high temperature ashing caused the V_2O_5 to fuse on the crucible wall making complete removal extremely difficult. Any loss of material in this manner would, of course, lower the vanadium analysis.

TABLE 6.9

Effect of Ashing Method on Vanadium Analysis by Atomic Absorption

Sample Identification	Wt. % Vanadium in Sample	
	Ashing at High Temp.*	Liquid Fire
Run 34		
Firetube Deposit	4.7	7.8
Pass 2 Deposit	9.3	9.2
Pass 3 Deposit	2.3	6.2
Pass 4 Deposit	3.7	4.7
Run 33		
Firetube Deposit	-	7.5
Pass 2 Deposit	-	8.2
Pass 3 Deposit	3.9	4.3
Pass 4 Deposit	4.3	4.8

*Ashed at 1450°F overnight.

Arc Emission Spectroscopy was also evaluated as an alternate means of instrumental analysis. The major advantage of this method is the ability to obtain multi-element analysis on the same sample. The primary disadvantage is that a much larger sample is required than with Atomic Absorption. In this study, the firetube deposit from a third experiment, run 40, was used. Since there appeared to be pieces of refractory from the combustion chamber contaminating the sample a simple sieving separation was employed. To provide a homogenous sample, only material passing through a -200 mesh standard sieve (~75 μm) was used. This amounted to roughly 95% of the total. Ten separate samples were analyzed using the spectrometric procedure. Ten other samples of the sieved material were analyzed using liquid fire/Atomic Absorption. A comparison of the results are presented in Table 6.10. The two methods showed good agreement and both had satisfactory precision.

TABLE 6.10

Comparison of Instrumental Methods of Vanadium Analysis

	Emission Spectroscopy	Atomic Absorption
	6.8	6.6
	6.8	6.7
	6.9	6.6
	6.7	6.8
	6.4	6.8
	6.8	6.5
	6.8	7.1
	6.5	6.1
	6.6	7.0
	6.9	6.9
$\bar{x}$	6.7	6.7

Emission Spectroscopy:

$\sum (x-\bar{x})^2 = 0.26$

$s = \sqrt{\frac{0.26}{9}}$

$s = 0.17$

$= \pm 2.5\%$

Atomic Absorption:

$\sum (x-\bar{x})^2 = 0.73$

$s = 0.27$

$= \pm 4.0\%$

In Table 6.11 the complete multi-elemental analysis obtained using Emission Spectroscopy has been summarized. The first determination was made on the fire chamber sample before sieving. The ash level is significantly higher, which may be attributed to refractory material rich in silica and probably some rust particles. After sieving, the ash determinations were quite uniform. The ratio of Ni to V in the sample is on the same order as in the residual fuel oil; Na content, however, is slightly higher.

To complete the analytical procedure, a method was developed that permitted quantitative extraction of vanadium from the particulate collected on a standard EPA-type, fiber glass filter mat. The fiber glass filter was supplied by Western Precipitation as a part of their stack sampler (Emission Parameter Analyzer) and was stated to be equivalent to MSA-1106BH. In practice, the glass filter (125 mm) after being cut into strips was extracted with a heated solution of 5% nitric acid for about one hour. The solution was filtered to remove carbonaceous residue and then analyzed by Atomic Absorption. The vanadium content is obtained by relating the measured absorbance of the solution to the absorbance of standard solutions. To insure that the filter itself did not contain appreciable vanadium several blanks were run. The results were all negative. In this respect, the filter may be similar to the spectro grade type A glass fiber filter distributed by Gelman Instrument Company. Based on a product description bulletin, for the typical 8" x 10" filter sheet V content is <10 μg.

Carbonaceous particulate remaining from the extraction process was similarly analyzed for vanadium. The solids were first digested using liquid fire and then analyzed by Atomic Absorption. Vanadium content proved to be negligible, amounting to <0.2% of the total vanadium associated with the filter particulate.

TABLE 6.11

Elemental Analysis by Emission Spectroscopy
(Run 35, Fire Chamber)

Determination		Ash*%	Fe %	Si %	Ni %	Na %	V %
1		35.2	8.5	0.4	0.9	0.9	6.9
2	After sieving thru 200 mesh	31.4	8.3	<0.2	1.1	0.9	6.8
3	" "	30.9	8.2	<0.2	1.1	0.9	6.8
4	" "	31.2	8.3	<0.2	1.0	0.9	6.9
5	" "	30.7	7.8	<0.2	1.0	0.9	6.7
6	" "	31.0	7.7	<0.2	1.0	0.9	6.4
7	" "	30.9	8.2	<0.2	1.1	0.9	6.8
8	" "	31.1	8.3	<0.2	1.1	0.9	6.8
9	" "	31.3	8.2	<0.2	1.0	0.9	6.5
10	" "	30.9	8.1	<0.2	1.0	0.9	6.6
11	" "	31.0	8.6	<0.2	1.1	0.9	6.9

*Ashed at 1450°F

7. RESULTS AND DISCUSSIONS

7.1 Basis for Comparing Vanadium Recovery

This section discusses the results of the factorial test program to measure vanadium particulate collection efficiency of the EPA Method 5 sampling train and compare it with the ER&E developed system. The operating data for the 32 tests constituting this program are presented in Appendix 4 Tables 1-10. Complete particulate and vanadium inventories are presented in Appendix 5 Tables 1-12. This section also discusses the several experiments run to determine changes in oxidation state of selected vanadium compounds exposed for several hours to flue gas at elevated temperatures.

The strategy for establishing vanadium collection efficiency was based on making a vanadium material balance around the boiler. The elements of this balance involved establishing the amount of vanadium entering the boiler from the fuel and then comparing it with the amount of vanadium collected in the solids deposited in the boiler passes plus the amount collected in the respective stack sampling train. The amount of vanadium entering the boiler was easily determined knowing the fuel firing rate and vanadium analysis of the oil. The amount deposited in the boiler was based on collection of all deposits from the tube inserts as discussed in section 6.4. The amount sampled in the stack, however, represents only a small portion of the total vanadium being carried in the flue gas leaving the boiler and is normally expressed in terms of concentration, i.e. mg/SCM, flue gas. To relate this fraction to the total volume of flue gas produced during combustion in these experiments, a stoichiometric calculation was made based on the elemental analysis of the fuel and the excess combustion air. Since the three test fuels which were used had fairly similar C/H ratios, the amount of combustion gas produced per pound of fuel fell within a narrow range; 195-200 SCFDB/lb. fuel at 110% of stoichiometric air. Using this relationship, it is possible to convert particulate concentration expressed as mg/SCM into weight percent on fuel burned, and hence into part per million (ppm), on a fuel basis. This latter nomenclature is used throughout this report to express vanadium content in particulates. The concentration of particulate in flue gas has also been corrected to a standard basis of 3% O_2 at 1 atmosphere pressure and 77°F. In addition all gas volumes are reported on a dry basis (i.e. SCMDB).

7.2 Vanadium Material Balance Around the Cleaver Brooks Boiler

7.2.1 Total Vanadium Recovery Using All-Venezuelan Resids

This section compares the overall vanadium balance around the Cleaver Brooks boiler which then provides the basis for comparing the collection efficiency of the stack sampling systems. The results are illustrated graphically in Figures 7.1 - 7.3. Vanadium recovery, which is defined as the amount of vanadium recovered in the boiler plus the amount of vanadium recovered in the respective stack sampling systems as a percent of the vanadium input from the fuel, is represented in bar chart form as a function of fuel type and combustion conditions. At high firing rate (short combustion chamber residence time, τ_o), total vanadium recovery from the all-Ven (Venezuelan) fuels (F_1 and F_2) ranged between 58 wt. % and 104 wt. %. The combined average, however, based on the 24 runs made with both sampling systems in this block of the study amounted to 85.3 wt. % ± 3.7 (95 percent confidence limit). This recovery is excellent and probably represents the best that may be obtained in our system. For example, consider that the vanadium inventory in the boiler made no allowance for possible V fallout at the two headers. Additionally vanadium recovery was based on the analysis of vanadium in a minimum of ten separate particulate samples and that each of these measurements had an associated precision of ± 4.5%. Comparing the two stack sampling system invididually, it is readily apparent that Method 5 recovered on average more vanadium, 88.6 wt. % than the ER&E system, 81.8 wt. %.

At this combustion condition, the amount of vanadium collected in the boiler was fairly consistent averaging 29.3 wt. %. This represents about one-third of the total vanadium recovered. The stack sampling systems had combined recovery of 56.0 wt. %.

At the low firing rate (residence time was increased by a factor of almost 7), vanadium inventoried in the boiler passes plus the stack sampling systems was significantly lower. Total vanadium recovered amounted to 68.1 wt. % ± 3.7 (95 percent confidence limit). This represents a decline of 20% relative to the low firing rate runs (long residence time). This may be observed in Figure 7.2. Vanadium recovered in the boiler averaged 22.7 wt. % versus 29.3 wt. % in the previous series of runs. The reason for the reduction in the amount of vanadium fallout in the boiler passes is not understood. It may be speculated that the low volumetric flow rate of the combustion gases at reduced firing results in a maldistribution of the combustion products as they go through the passes. Since only one insert was used per pass to collect the vanadium-bearing particulate, any maldistribution would easily upset the inventory. These points will be amplified at greater length in section 7.5, where vanadium recovery in the boiler is considered in detail. The main point to be noted here, however, is that a decrease in V recovery in the boiler affects the material balance and has a disproportionate effect on sample system collection efficiency because of the difference in bases used for the comparisons.

FIGURE 7.1

TOTAL VANADIUM RECOVERED IN BOILER AND STACK-SHORT RESIDENCE CASE

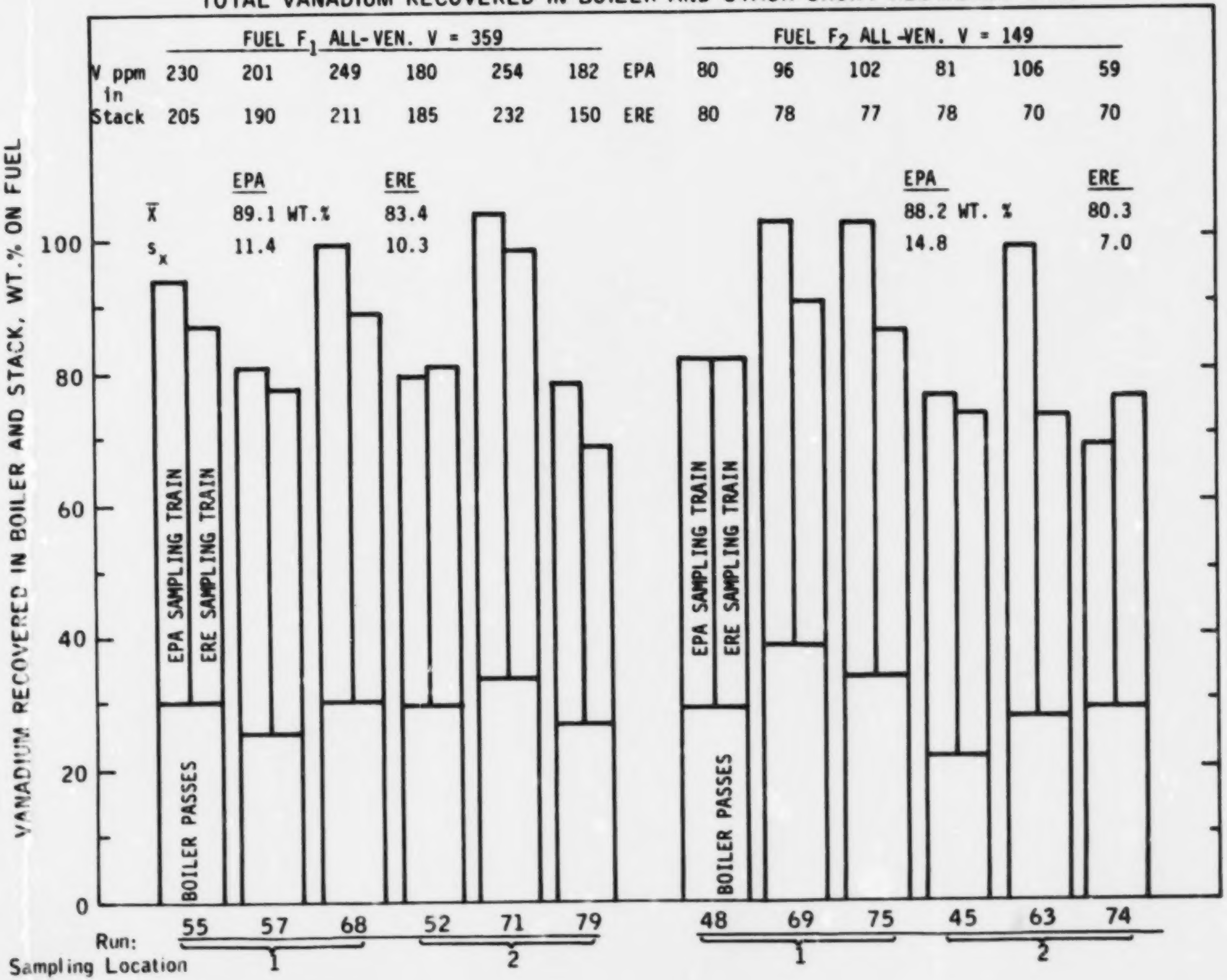
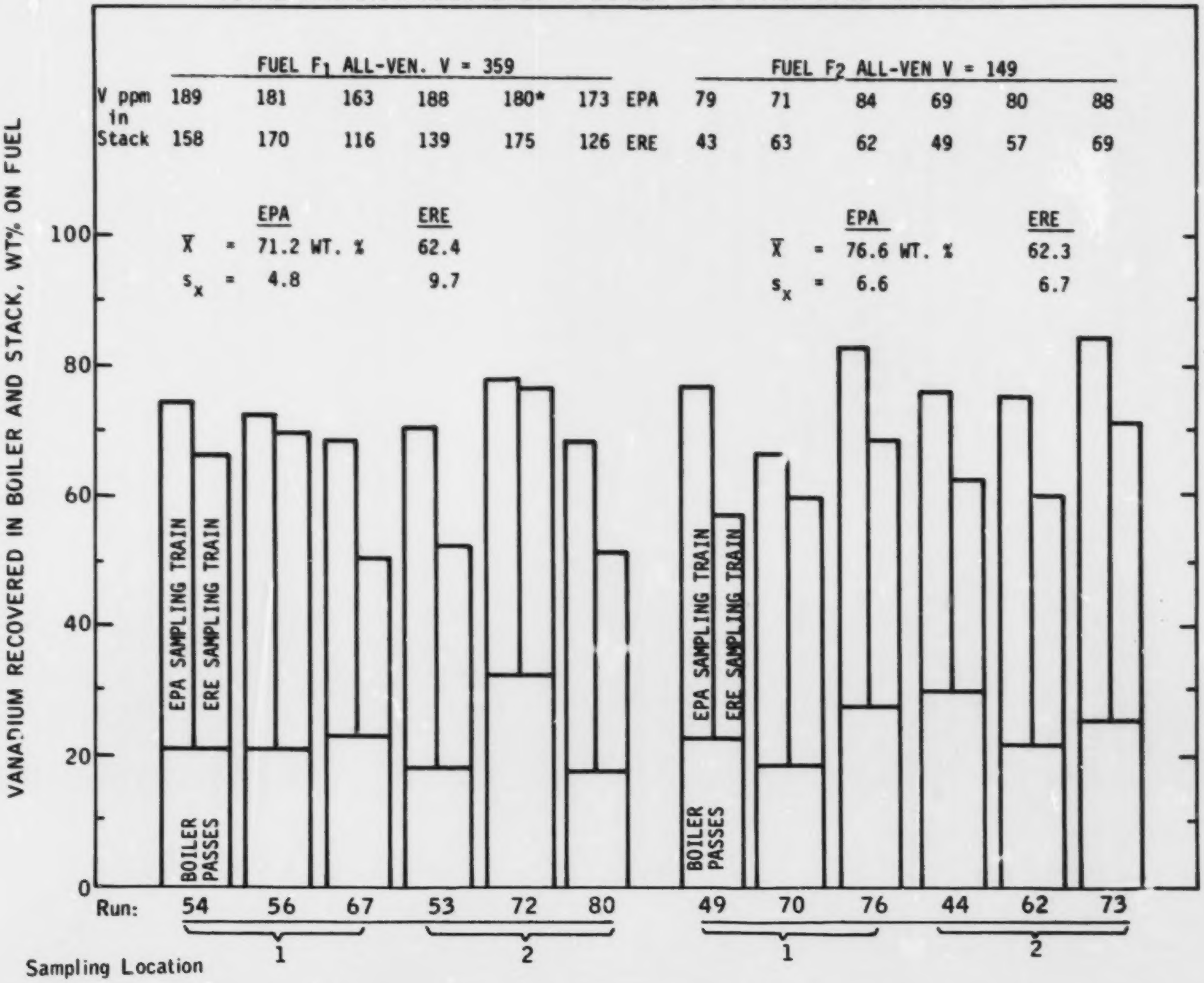


FIGURE 7.2

TOTAL VANADIUM RECOVERED IN BOILER AND STACK-LONG RESIDENCE CASE



The stack sampling system accounted for most of the decrease (∿60%) in vanadium recovery. The combined average for both EPA and ER&E trains amounted to 45.4 wt. % representing a decline of 19% relative to recovery at the high firing rate (τ_o) runs. The ER&E train showed the lowest recovery of vanadium averaging 39.5 wt. %, exclusive of the boiler inventory. In contrast, the EPA system averaged 51.2 wt. %. The difference between the two systems, roughly 25%, represents a measure of collection inefficiency - the inability to collect fine particles of vanadium. It is evident that the silicone oil-impingers of the ER&E system do not collect all the fine vanadium-bearing particles which pass the last stage of the Andersen Cascade Impactor. The latter has a size cut-off (d_{50}) of roughly 0.4 microns. These fine particles also appear to pass through the dry ice-acetone cooled condenser.

The inefficiency of the Greenberg-Smith type impingers to collect fines is not attributable to use of only our liquid medium but appears to be general since the same problem was encountered with the water impingers used in Method 5. Fine V particles which are capable of passing through the fiber glass filter (MSA-1106BH) also pass cleanly through the impingers. This was particularly apparent at long residence time where at most only a few ppm of vanadium were ever isolated from the impingers even though up to 20% more vanadium fines (by weight) appeared to have passed through the filter. Relative to the combination of Cascade Impactor/impingers, the filter has a lower particle size cut-off thus it collects more of the vanadium-bearing submicron particulate.

7.2.2 Erratic Vanadium Recovery Using Light Arab Residuum

The runs made with the light Arab fuel oil at both high and low firing rates were characterized by extreme fluctuations in vanadium recovery and generally poor reproducibility. As illustrated in Figure 7.3 with the exception of a few runs most of the inventories were over 100%. At the high firing rate (τ_o) recovery in the boiler ranged from 36 wt. % to 67 wt. % and over the five runs averaged 51.3 wt. %. This was significantly higher than the inventory obtained with either of the all-Ven fuel oils. Recovery of vanadium in the stack, based on the combined sampling systems, averaged 71.5 wt. %. Taken together, the total of boiler and stack inventories equaled 122.8 wt. % ± 18.8 (95 percent confidence limit). The confidence limits are directly proportional to the spread of the data and therefore serve as a measure of experimental error. The lack of run to run reproducibility is indicated by the large limits placed around the average ± 18.8%.

At the reduced firing rate (τ_1) recovery in the boiler was somewhat more uniform but still substantially lower than that at the higher firing rate. Directionally, these results confirm the difference noted in boiler inventory with the two all-Ven fuels fired at the respective combustion conditions. The V inventory from the various passes in the boiler averaged 32.3 wt. % and the stack sampling systems averaged 73.2 wt. %. Total recovery therefore equaled 105.5 ± 28.4% (95 percent confidence limit). The large experimental uncertainty is associated in this case with the stack sampling systems, particularly the inventory made in Run 51 where recovery amounted to 174% (ER&E system) versus 87.1% (Method 5).

Since results obtained in the tests with light Arab fuel were so erratic, it served no useful purpose to carry them through a statistical analysis. Therefore, this test series was not included in the overall analysis of variance (ANOVA).

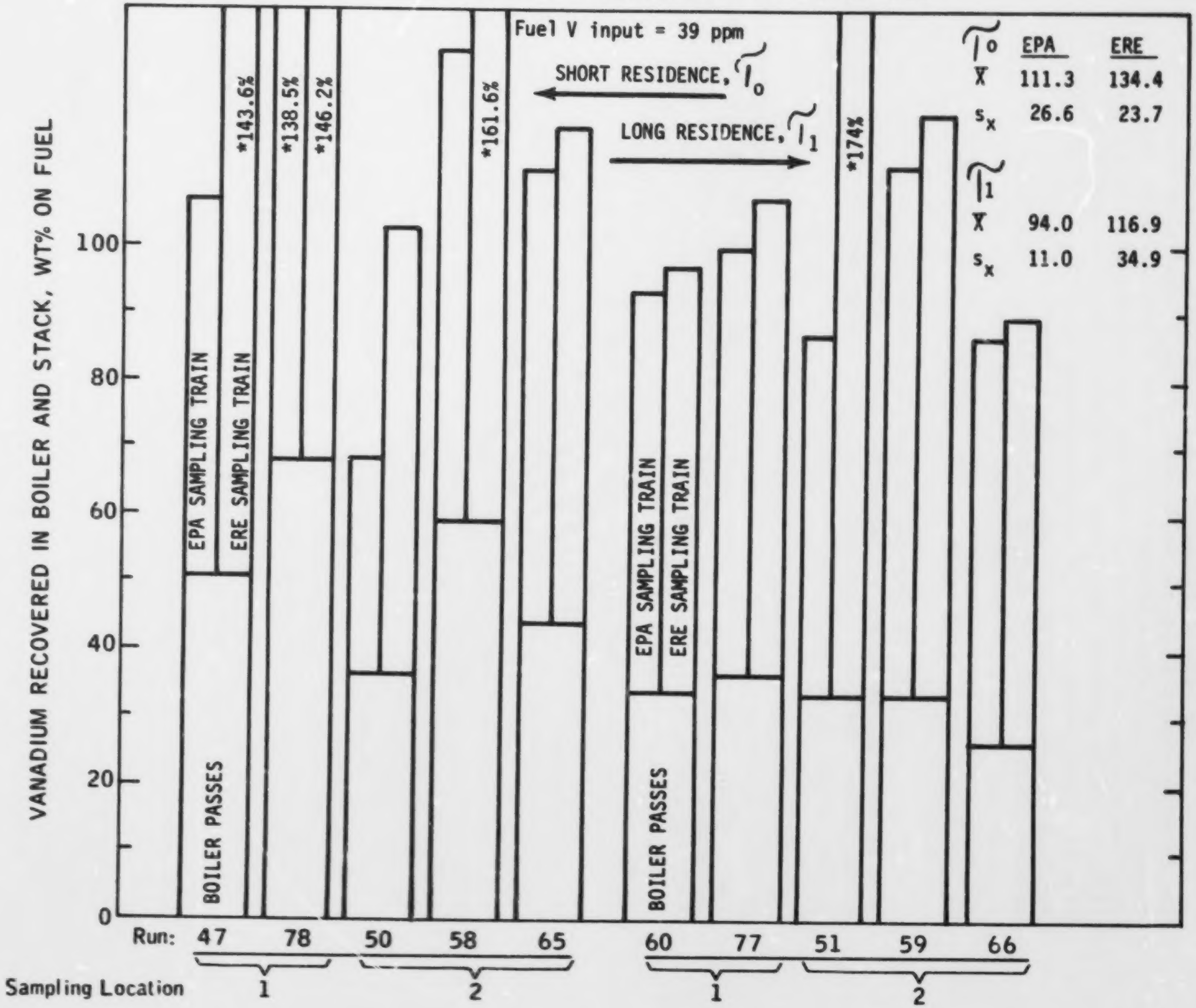
The very low vanadium content in the particulate is probably the main cause for the large fluctuations observed in these runs. Since V inventory in these tests was based on the sum of the individual V analyses of a large number of different samples, handling and/or analytical errors were probably compounded. For example, tests conducted at high firing rates (short residence time), showed the largest absolute variation in the amount of V collected. Solids deposited in the boiler varied by as much as 12 ppm (on fuel) or roughly 30% of total V input from the fuel. In the stack, the range was about 15 ppm. At this combustion condition, a large amount of carbonaceous particulate was emitted; the boiler and stack solids totaled 361 mg/SCM, equivalent to 0.46 wt. % on fuel. Included in this total was the fuel ash which accounted for about 0.01 wt. % or roughly 2% of the particulate weight. Since the carbonaceous particles each contain some ash, the concentration of vanadium in the particulate was low (i.e. the V content in the solids averaged about 1.0 wt. %).

At long residence time, 79% of the carbonaceous solids were consumed. This resulted in a particulate inventory of 77 mg/SCM; equivalent to 0.10 wt. % on fuel. The concentration of ash in the particulate was increased to 10%. The average vanadium content in the solids amounted to 7.8 wt. % compared to 1.0 wt. % at the short residence time. While the vanadium content was higher, the weight of solids collected was quite low. This latter proved to be a limiting factor, affecting sensitivity of the analtytical method. These data are summarized in Table 7.1.

Comparing the stack particulate inventory made with the entire ER&E system but only the front half of the Method 5, there was excllent agreement. The largest difference between the two sampling trains occurred at the high firing rate (short residence) and amounted to 16 mg/SCM or about 7% on total weight. At the low firing rate

FIGURE 7.3

TOTAL VANADIUM RECOVERED-LIGHT ARAB FUEL



(long residence) where particulate emissions were lower, a relative difference of about 4% (1 mg/SCM) was obtained.

The back half or impinger part of the Method 5 train was also found to contain solids. However, it was determined that this material, consisting mostly of sulfate, was an artifact of the chilled water impingers. In runs made with the two all-Ven fuels, the same type solids in varying amounts were also isolated from the water impingers. Since these solids were not real particulate emitted during combustion of fuel oil, they were not counted in the total inventory. A more detailed discussion of the nature of these artificial particulates is presented in section 7.7.

7.2.3 Statistical Analysis to Compare Vanadium Recovery

An analysis of variance (ANOVA) was made to compare the influence of stack sampling system (S) fuel oil (F), combustion chamber residence time (T), and port location in stack (L), on total vanadium recovery. The ANOVA which is presented in Table 7.2 indicates that fuel type and sample port location are not statistically significant and therefore do not affect vanadium recovery. The main effects, as indicated by the F ratio in excess of the critical table value $P(F > 5.57) = 0.05$ at ϕ_1, ϕ_{32} (degrees of freedom) are residence time and sampling system. Since there were no significant interactions, vanadium recovery may simply be represented as a function of these two variables. The effect of residence time (τ) is to reduce vanadium recovery by 20% and this appears to be independent of the tested levels of the other variables (none of the interactions T·F, T·S, T·F·S, T·L, T·S·L, T·F·S·L are large). The effect of sampling system(S) is to reduce vanadium recovery by 11% (81.3 wt. % to 72.1 wt. %) and this also appears to be independent of the tested levels of the other variables (none of the interactions T·S, F·S, T·F·S, S·L, T·S·L, F·L·S, T·F·S·L are large). Residence time, with one degree of freedom, accounted for 42.6% of the total experimental variation (sum of squares/total error). Residence time (τ) and sampling system (S) combined,with two degrees of freedom, accounted for more than half of the variation, 54.8%. Pure experimental error (residual effect) estimated with 32 degrees of freedom amounted to 35.1% of the total variation. The remainder was associated with the interaction effects which were very minor, amounting to 10.1% of the total calculated experimental variation.

Pooling the two nonsignificant variables, fuel and port location, a two way analysis of variance was made to obtain a better estimate of experimental precision. The new variance with 44 degrees of freedom was 83.31 whereas the previous variance had 32 degrees of

TABLE 7.1

AVERAGE PARTICULATE AND VANADIUM INVENTORY FOR LIGHT ARAB FUEL

Particulate Distribution	Short Residence Time Particulate mg/SCM	Short Residence Time Vanadium Analysis wt. %	Short Residence Time Vanadium Content ppm (on fuel)	Long Residence Time Particulate mg/SCM	Long Residence Time Vanadium Analysis Wt. %	Long Residence Time Vanadium Content ppm (on fuel)
• Boiler Solids	154	1.02	20	50	2.04	13
• Stack Particulate						
- ER&E Train						
>10μm	59	0.53	4	3	2.61	1
1-10μm	106	0.67	9	5	1.57	1
<1μm	50	2.98	19	19	14.46	35
Total	215		32	27		37
- EPA Train						
Probe & Cyclone	98	0.64	8	5	1.57	1
Filter	101	1.09	14	23	7.51	22
	(199)		(22)	(28)		(23)
Water Impingers	12		Trace	11		Trace
Total	211		22	39		23

NOTES:

(1) All data corrected to 3% O_2.

(2) Results from individual runs summarized in Tables 9-12 , Appendix 5.

freedom and was equal to 90.61. The twelve additional degrees of freedom permitted by folding over the factorial design gave about an 8% improvement in estimating the experimental precision.

The relative variance (percent of the total experimental variance of 83.31) associated with vanadium recovery in the boiler passes amounted to 23%, while the variance associated with vanadium recovery in the stack (both sampling systems) accounted for 59%. The remainder, 18%, was the unexplained variance and represented the sum of all unaccountable experimental errors, i.e. errors attributed to sampling, handling and V analysis. It may be noted that the stack measurement part of the experiment had the lowest precision. However, this represents the totality of all treatments, a large part of this was probably associated with the decrease in ER&E system collection efficiency particularly at the low firing rate (Υ_1).

The highest vanadium recovery was obtained using the EPA Method 5 train at short combustion residence time. Total recovery as summarized in Table 7.3 averaged 88.6 wt. % ± 5.2 (95 percent confidence limit). This value which was based on an overall vanadium material balance conducted around the boiler probably represents close to quantitative recovery of V considering the number of measurements that were involved and the potential inaccuracies. In comparison vanadium recovery based on the ER&E stack sampling system was lower by 7.7% and averaged 81.8 wt. % ± 5.2 (95 percent confidence limit). The difference in averaged recovery between the two sampling systems was not found to be significant at the 95 percent level using "Student's t-test". However, when tested at the 90 percent level the difference was significant. Overall, the two sampling trains gave acceptable vanadium recovery.

At long combustion chamber residence time, vanadium recovery measured by either stack sampling system was significantly lower, however, the decrease obtained in the ER&E system was much greater. Based on Method 5, total V recovery went from 88.6 wt. % to 73.9 wt. % ± 5.2 (95 percent confidence limit) representing a relative decrease of 16.6% Based on the ER&E system, recovery was decreased by 24%, to a level of 52.3 wt. %. Comparing the two sampling systems the change in vanadium recovery amounted to 16%.

7.2.4 Vanadium-Bearing Particulate Inventory

Although the amount of vanadium collected by the sampling systems was different, the total amount of particulate collected was similar and well within experimental error. For the high ash (V = 359 ppm) all-Ven fuel oil (F_1) presented in Table 7.4 at short residence time, total particulate emissions inventoried in the ER&E stack sampling system amounted to 305 mg/SCM equivalent to 0.39 wt. % on fuel oil. The Method 5 train collected 301 mg/SCM equivalent to 0.38 wt. % on fuel oil. The vanadium content in the total particulate

TABLE 7.2

ANALYSIS OF VARIANCE - TOTAL VANADIUM RECOVERY IN BOILER AND STACK

LEVELS OF FACTORS

T	T_0, T_1	2	Residence Time
F	F_1, F_2	2	Fuels (Ail-Van)
S	EPA, ERE	2	Sampling Train
L		2	Sampling Location in Stack
R	1 2	3	Replications

FACTOR	MEANS FOR EACH LEVEL, VANADIUM RECOVERY WT. %		
T	85.258	68.124	
F	76.554	76.829	
S	81.283	72.099	
L	78.558	74.824	
R	74.312	80.174	75.587

$S.E = \sqrt{90.61/24} = 1.94$

GRAND MEAN = 76.691

SOURCE OF VARIATION	SUMS OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARES	F RATIO	Critical Table Values 95% Confidence (F.05)
T (RESIDENCE TIME)	3522.61182	1	3522.61182	38.88	5.57
F (FUEL)	0.90749	1	0.90749		
TF	65.80082	1	65.80082		
S (SAMPLING SYSTEM)	1012.00354	1	1012.00354	11.17	5.57
TS	68.16337	1	68.16337		
FS	44.46763	1	44.46763		
TFS	7.84080	1	7.84080		
L (PORT LOCATION)	167.25323	1	167.25323	1.84	5.57
TL	280.33355	1	280.33355	3.09	5.57
FL	19.00084	1	19.00084		
TFL	166.50759	1	166.50759	1.83	5.57
SL	5.60334	1	5.60334		
TSL	6.45336	1	6.45336		
FSL	1.84081	1	1.84081		
TFSL	0.18749	1	0.18749		
RESIDUAL ERROR	2899.61118	32	$90.61 = s^2$		
TOTAL	8268.60158	47			

Conc: Only Residence Time And Sampling System have An effect on V recovery.

TABLE 7.3

TOTAL VANADIUM RECOVERY AS AFFECTED BY STACK SAMPLING SYSTEM AND COMBUSTION CHAMBER RESIDENCE TIME

	EPA Method 5	ER&E Train	t Test
τ_o (Short Residence Time)	88.6 wt. % (83.4 - 93.8 wt. %) = P (.95)	81.8 wt. % (76.6 - 87.0 wt. %) = P (.95)	t calcd. = 1.54 ϕ = 44 At 95%, Critical Table Value = 1.96 Difference not significant At 90% difference is significant
τ_1 (Long Residence Time)	73.9 wt. % (68.7 - 79.1 wt. %) = P (.95)	62.3 wt. % (57.1 - 67.5 wt. %) = P (.95)	t calcd = 4.41 ϕ = 44 At 95%, Critical Table Value = 1.96 Difference is significant

NOTE:

Experiment variance = $s^2 = 83.31$

Standard error = $s_x = \sqrt{\frac{s^2}{K = 12}} = 2.63$

95 percent confidence interval = t (.025,44) = 1.96 x 2.63 $\pm \overline{X}$

Probability $-5.2 \leq \overline{X} \leq +5.2 = 0.95$

TABLE 7.4

AVERAGE PARTICULATE AND VANADIUM INVENTORY
HIGH ASH ALL VENEZUELAN FUEL OIL (F_1)

	Short Residence Time			Long Residence Time		
Particulate Distribution	Particulate mg/SCM	Vanadium Analysis wt. %	Vanadium Content ppm (on fuel)	Particulate mg/SCM	Vanadium Analysis wt. %	Vanadium Content ppm (on fuel)
● Boiler Solids	222	3.68	104	61	9.91	77
● Stack Particulate						
- ERE Train						
>10μm	104	1.81	24	3	5.23	2
1-10μm	145	5.36	99	12	15.04	23
<1μm	56	10.09	72	48	19.95	122
Total	305		195	63		147
- EPA Train						
Probe and Cyclone	184	2.43	57	7	3.36	3
Filter	117	10.67	159	65	21.26	176
	(301)		(216)	(72)		(179)
Water Impingers	8		Trace	5		Trace
Total	309		216	77		179

NOTES:

(1) All data corrected to 3% O_2.

(2) Results from individual runs summarized in Tables 1-4 , Appendix 5.

collected by the ER&E train averaged 5.02 wt. % compared to 5.63 wt. % in Method 5. On an absolute basis, this difference amounted to 21 ppm V and was mainly associated with the filter catch. Typically the smallest sized particulate have the highest vanadium contents. In this case, however, the particulate on the filter had a higher V concentration than particulate isolated in the submicron size range, 10.67 wt. % versus 10.09 wt. % V. While this may appear paradoxical, the situation could arise if the filter collected finer submicron particles than the impingers, i.e., the filter had a much lower size range cut-off. If it is assumed that the missing 21 ppm of vanadium (as V_2O_5) passed through the ER&E system, then the difference in particulate inventory necessary to account for it would amount to about 3 mg/SCM. Even if the V content in the missing particulate was 10.09 wt. %, the difference would amount to only about 17 mg/SCM or about 7% on the total inventory. This magnitude is well within the expected experimental variation and would not be detected.

Some insight into the nature of particulate emissions was obtained in previous company sponsored studies. Table 7.5 shows the C, N and ash composition of the particulate in the different size ranges.

TABLE 7.5

PARTICULATE COMPOSITION INFLUENCED BY SIZE
(High Sulfur Fuel Oil)

Particulate Fraction	Analysis, wt. %		
	Carbon	Nitrogen	Inorganic Ash
>10 micron	79.4	1.8	10.1
1-10 micron	70.7	1.2	18.1
<1 micron	30.1	0.3	57.1

The largest particles, mostly cenospheres, have a high carbon content, 79.4%, and a relatively low ash content, about 10%. The intermediate size range has a slightly lower carbon content and a somewhat higher ash content, about 18%. The submicron particles have a relatively low carbon content, only 30.1% and a much higher ash content, about 57%.

Analysis of the ash residue from the three size ranges, Table 7.6 indicated that a large part of each was vanadium. Expressed relative to fuel oil the vanadium oxide in the particulate ranged from as little 24 ppm in the very large particles to 137 ppm in the smallest particles.

TABLE 7.6

DISTRIBUTION OF V_2O_5 IN PARTICULATE ASH

	Wt. % in Ash Fraction			Wt. % on Fuel in Size Range		
	>10	1-10	<1	>10	1-10	<1
V_2O_5	41.6	63.7	58.2	.0024	0.0110	.0137
Na_2O	1.7	1.8	3.4	.0002	.0003	.0008

At long residence time, the total difference in particulate inventory between the two sampling systems amounted to about 14%, which on an absolute basis was only 9 mg/SCM. The ER&E system collected 63 mg/SCM of particulate,(0.08 wt. % on fuel)versus 72 mg/SCM (0.09 wt. % on fuel)for Method 5. The net effect of increased residence time is that most of the carbonaceous residues burn-out, so that the total weight of particulate is substantially reduced. Additionally, the size distribution of these particles is shifted toward the submicron range. Ash material, mainly vanadium oxide, which would normally have been distributed among the carbonaceous particulate is probably vaporized into the combustion gas stream, then recondenses in the cooler part of the boiler as submicron particles. As may be noted in Table 7.4, about 83% of the vanadium particles collected by the ER&E sampling system were in the submicron size range compared to 37% at short residence time. This shift in size distribution is also borne out by the Method 5 train. Vanadium collected on the glass filter (<5 micron) amounted to 74% at short residence time compared to 98% at long residence time. The concentration of vanadium in the fine particulate was also substantially higher than in the previous runs at τ_o. Submicron particulate collected in the silicone oil impingers had a vanadium content of 20 wt. % and those collected on the fiber glass filter had a V content of 21.3 wt. % versus roughly 10.5 wt. %. Since the concentration of

V in the particulate is high, the loss of only a small amount of these fine particles may have a critical effect on the overall V recovery. For example, the difference between sampling system particulate inventory amounted to 9 mg/SCM or on a relative basis about 14%. If the vanadium content in this amount of particulate was roughly 27 wt. %, which is not much higher than the concentration actually assayed, it would account for the 34 ppm difference obtained in vanadium inventory. On the other hand in the Method 5 sampling system, if the fines which passed through the filter were V_2O_5, an increase in total particulate inventory of about 10% would be sufficient to bring vanadium recovery up to 90%.

In tests made with the intermediate ash, all-Ven fuel oil (F_2) summarized in Table 7.7, total particulate collected by Method 5 (front half only) and ER&E stack sampling trains also showed good agreement. Directionally the results were very similar to those obtained with fuel F_1. At short residence time particulate inventories were identical, 127 mg/SCM versus 128 mg/SCM, equivalent to 0.16 wt. % on fuel oil. However, the average vanadium content was higher in the solid collected by Method 5, 4.64 wt. % versus 5.34 wt. %. This difference on an absolute basis amounted to 12 ppm V or roughly 15% of the total inventoried in the stack. Again, it may be concluded that the loss of vanadium from the ER&E train was associated with the passage of a relatively small amount of fine, vanadium-bearing particulate out the impingers. This situation also occurred in the runs made at long residence time. However, in this case, it was further aggravated by the shift in size distribution to nearly all submicron particles and the higher vanadium content in these fines. The EPA system collected about 13% more particulate, which on an absolute basis amounted to 5 mg/SCM. The vanadium content in the particulate was also higher averaging 14.93 wt. % versus 12.43 wt. %.

7.2.5 Size Distribution of Vanadium-Bearing Particulates

The size distribution of the vanadium-bearing particulate which deposited in the boiler was also influenced by combustion conditions. At short residence time, the vanadium content in these deposits averaged 3.9 wt. %. Based on a similar concentration in the stack, 3.3 wt. %, the particulate were predominantly in the 1-10 micron size range. At long residence time, the boiler deposits averaged 7.6 wt. %, indicating a mix of submicron and 1-10 micron particles.

The size distribution of particulate in the stack as previously noted was significantly altered by combustion conditions. The results which have been determined with the ER&E sampling train are summarized in Table 7.8. At short residence time, irrespective of fuels, approximately 29% of the total particulate weight was emitted as cenospheres (>10 microns) while 76% of the particulate was emitted in the size range >1 micron. Submicron particulate amounted to 24% of the emissions. At the increased residence time, combustion of the

TABLE 7.7

AVERAGE PARTICULATE AND VANADIUM INVENTORY INTERMEDIATE ASH ALL VENEZUELAN, FUEL OIL (F_2)

	Short Residence Time			Long Residence Time		
Particulate Distribution	Particulate Mg/SCM	Vanadium Analysis wt. %	Vanadium Content ppm (on fuel)	Particulate Mg/SCM	Vanadium Analysis wt. %	Vanadium Content ppm (on fuel)
• Boiler Solids	89	3.88	44	37	7.64	36
• Stack Particulate						
- ERE Train						
>10μm	30	1.57	6	4	1.96	1
1-10μm	57	3.30	24	7	5.61	5
<1μm	40	8.83	45	25	16.01	51
Total	127		75	36		57
- EPA Train						
Probe and Cyclone	51	2.00	13	5	1.57	1
Filter	73	7.96	74	36	16.79	77
	(128)		(87)	(41)		(78)
Water Impingers	13		Trace	10		Trace
Total	141		87	51		78

NOTES:

(1) All data corrected to 3% O_2.

(2) Results from individual runs summarized in Tables 5-8, Appendix 5.

TABLE 7.8

RELATIVE SIZE DISTRIBUTION OF STACK PARTICULATE

NOTE: Based on Data From ER&E Sampling System

Size Distribution	Short Residence Particulate, %	Short Residence Vanadium, %	Long Residence Particulate, %	Long Residence Vanadium, %
	Fuel F_1 - High Ash, All-Ven			
>10μm	34	12	5	1
1-10μm	48	51	19	16
<1μm	18	37	76	83
	100	100	100	100
	Fuel F_2 - Intermediate Ash, All-Ven			
>10μm	24	8	11	2
1-10μm	45	32	19	9
<1μm	31	60	70	89
	100%	100%	100%	100%
	Fuel F_3 - Low Ash, Light Arab			
>10μm	28	13	11	3
1-10μm	49	28	18	3
<1μm	23	59	71	94
	100%	100%	100%	100%

carbonaceous residues was facilitated and resulted in a pronounced shift in particle size distribution to the submicron range. At this condition, roughly 72% of the total particulate were emitted as submicrons compared to 24% in the previous run. The amount of cenospheres was decreased by almost 70% and now accounted for only 9% of the total weight. As cenosphere and cenosphere derived-residue burn out the volatile ash material present in these particles, particularly vanadium, is liberated into the gas stream to condense in the cooler part of the boiler as fine particles. Only 2% of the vanadium remained associated with these large particles compared to 11% at the short residence time. Approximately 12% of the vanadium was in >1 micron particles while 88% was in the submicron particles. From the preceding it may be concluded that at the long residence time, sampling system collection efficiency is influenced by the presence of a large amount of submicron particles.

7.3 Sampling System Collection Efficiency

Vanadium collection efficiency as used in this report is the ratio of the amount of vanadium collected in the stack sampling train divided by the amount of vanadium in the fuel minus the amount of vanadium that deposited in the boiler $\left(\frac{V_s}{V_F - V_B}\right)$.

Thus, it is apparent that for a particular level of vanadium recovery, the calculated collection efficiency will be lower because of the different basis used. Collection efficiency will be equal to 100% only if all of the vanadium introduced into the boiler from the fuel is recovered. Any vanadium which is not accounted for in the deposits from the passes is assumed to enter the stack. If the amount of vanadium inventoried by the stack sampling is insufficient to close the balance then the difference is attributed to the inefficiency of the collection system for collecting V fines. In this study, the highest vanadium recovery averaged 88.6 wt. % using the Method 5 train at short residence time. However, this probably represents the best material balance obtainable with the resources employed; primarily the boiler tube inserts. Consequently, there is little direct data to indicate where the loss of vanadium, in this particular case 11.4% of the input, has occurred. Assigning it entirely to the sampling system as has been done in Table 7.9, the resulting vanadium collection efficiency of 83.9% represents the minimum value for Method 5. If the entire loss of vanadium occurred in the boiler passes then collection efficiency of Method 5 would naturally amount to 100% and the other values could be scaled up accordingly. The change in collection efficiency from 83.9% with Method 5 to 74.3% with the ER&E train is a real effect. This difference is attributed to the inability of the hot silicone oil impingers to collect all of the very fine vanadium particles.

At long combustion chamber residence time, the collection efficiency of Method 5 decreased from 83.9% to 66.2%, roughly a change of 21%. However of this total, more than half, 14%, was related to a lower vanadium inventory in the boiler passes. If the same amount of vanadium had been deposited in the passes at both residence times,sampling system collection efficiency would be equal to 72.4%. The collection efficiency of the ER&E system relative to Method 5 decreased by an additional 23% to a level of 51.1%. At short residence time, the relative loss in efficiency was only 11%. The steeper decline in ER&E stack train performance at long residence time is associated with the emissions of significantly smaller vanadium particles which pass unchecked through the hot oil impingers. In contrast, the fiber glass filter used in Method 5 retains more of these fine particles. Vanadium fines which do pass through the filter are not collected in the water impingers again indicating the inefficiency of this type of system to collect submicrons.

To sum up, the fiber glass filter used in Method 5 train has a significantly lower particle size cut-off than the high velocity type Greenberg Smith impingers. With this type of filter, Method 5 collection efficiency for vanadium particles in combustion-produced flue gas will amount to, at the very least, 66-84%. Large boilers which normally have bigger combustion chambers and therefore longer combustion chamber residence time will tend toward the lower vanadium collection efficiency.

7.4 Vanadium Input - Fuel Analysis

The first element of the material balance involved establishing the vanadium content of the three fuel oils. Although each fuel was drawn from a bulk lot, they were segregated and stored in 55 gallon drums. Each test was run with a new drum of fuel oil. Thus over the course of the program 36 drums of oil were sampled and analyzed for vanadium content prior to use. As illustrated in Table 7.10 the all-Ven, high ash fuel designated F_1 had a vanadium content averaging 359 ppm ± 8.4 (95 percent confidence limit) which expressed as V_2O_5 accounted for about 70% of the fuel ash. Nickel,sodium and iron were the other components in the ash. The intermediate ash all-Ven fuel oil, F_2, had a vanadium content averaging 149 ppm ± 4.2 (95 percent confidence limit). Expressed as V_2O_5, it accounted for about 66% of the ash weight. The light Arab low ash fuel designated F_3 had an average vanadium content of 39 ppm ± 2.0 (95 percent confidence limit) accounting for about 70% of the ash, on the basis of V_2O_5. Relative analytical precision was about the same, roughly 4% for the vanadium analysis in the three fuels.

TABLE 7.9

SAMPLING SYSTEM COLLECTION EFFICIENCY

	EPA Method 5	ER&E
Short Residence Time, τ_o	83.9%	74.3%
Long Residence Time, τ_1	66.2%	51.1%

As the precision of these analyses represented drum to drum variation only, fuel samples were drawn periodically from one drum and analyzed. This procedure served to test the hypothesis that the drum samples came from the same population and therefore the average value was representative of the vanadium content in the test fuel lot. The mean, as shown in Table 7.11, for the 11 vanadium determinations was 351 ppm with a standard deviation of 23 ppm or on a relative basis, 6.5%. Thus from a statistical standpoint the value of 359 ppm representing the average of all drums adequately describes the vanadium content of test fuel F_1. By inference, the same holds true for fuels F_2 and F_3. The vanadium content of the fuel oil multiplied by the fuel consumption gives the vanadium input.

TABLE 7.10

Drum to Drum Variation of Vanadium Analysis
(Basis: Individual Drums of Fuel)

	Fuel F_1 All-Ven High Ash (V ppm)	Fuel F_2 All-Ven Intermed. Ash (V ppm)	Fuel F_3 Lt. Arab Low Ash (V ppm)
	350	158	39
	368	150	40
	350	158	42
	358	158	38
	358	150	40
	363	150	38
	343	150	38
	363	145	38
	383	145	40
	335	150	37
	365	138	37
	373	140	-*
Mean = $\bar{X}$ =	359.1	149.3	38.8
Std. dev. = s_x =	13.2	6.6	1.5
Std. Error = $s_{\bar{x}}$ =	3.8	1.5	0.5
Relative std. dev.	3.7%	4.4%	3.9%

Notes:

* Vanadium analysis reported in Run 58 was outside the statistical acceptance limits.(25)

TABLE 7.11

Variation of Samples Within A Drum of All-Ven Fuel Oil

Date:	8/21	9/23	10/24	11/27	12/31	1/30	1/2/20	2/28	3/28	4/30	5/30
V,ppm:	330	300	330	373	350	358	365	353	360	380	360

$\bar{X}_{11}$ = 350.8 ppm

s_x = 22.84

$s_{\bar{x}}$ = 6.9

Relative std. dev. = 6.5%

7.5 Vanadium Recovery in the Boiler

7.5.1 Preliminary Tests - Evaluation of Boiler Pass Tube Insers

Several preliminary runs were made to determine how well the heat exchanger tube inserts worked and if replication of particulate inventory was possible. Two removable tube inserts were randomly placed in each of the three heat exchanger passes. Tests were then made using firing rates of 1 lb./min. and 2 lbs./min. at 10% excess combustion air. Results are presented in Table 7.12 and indicate that the inserts provide a reliable measure of particulate fallout in the boiler. To facilitate comparisons, the weight of particulate was divided by the calculated combustion gas volume (~195 SCFDB/lb. fuel) then multiplied by the total number of tubes in the pass to give mg/SCMDB (corrected to 3% O_2). Runs 33 and 34 may be directly compared since a similar firing rate, 1 lb./min. was used.

The difference between tube inventories in the same pass ranged from less than 1% to as much as 13%. However, for all tests the average was 5%. Run to run variation of fallout averaged about 9%. This somewhat higher difference was most likely associated with some facet of boiler operation (i.e. slightly different firing rates, stability, etc.) rather than handling errors. The major variation in particulate fallout between runs occurred in pass 2. This pass had the most surface area and therefore was prone to fluctuations or changes in boiler operation. For example, comparing Run 33 with Run 35, the fuel firing rate was increased from 1 to 2 lbs./min. The largest change in particulate was in pass 2 where the amount of fallout tripled in weight.

In Run 35, the effect on particulate fallout on changing combustion chamber residence time may be noted. As a result of increasing the fuel firing rate and therefore decreasing residence time, the amount of solids deposited in the passes was doubled. Since burnout of a carbonaceous particle in the combustion zone of a boiler is believed to take place by diffusion of oxygen to the particles' surface - a fairly slow process, shortening residence time increases the probability that the particle will escape unburned.

TABLE 7.12

VARIATION OF PARTICULATE DISTRIBUTION IN BOILER (PRELIMINARY TESTS)

Pass	Run 33 Total Particulate/Pass mg/SCM*		Run 34 Total Particulate/Pass mg/SCM*		Run 35 Total Particulate/Pass mg/SCM*	
	A	B	A	B	A	B
Pass 1 (firetube)	40.1		42.3		82.2	
Pass 2	29.2	31.4	35.2	36.9	106.3	105.0
Pass 3	18.0	18.1	21.0	Sample Contaminated	36.9	32.3
Pass 4	11.7	12.9	12.0	12.1	1.3	1.4
Total	99.0	102.5	110.5		226.7	220.9
Fuel Consumption; Lb.						
- Inserts in Place	194.50		198.25		373.50	
- Total Run	320.50		305.75		556.25	
Firing Rate, Lbs./Min.	1		1		2	

*Corrected to 3% O_2.

Residence time also had considerable influence on the concentration and distribution of vanadium in the boiler solids. For a particular combustion condition, as shown in Table 7.13, there was little variation between runs in vanadium content of particulate from the same pass. On average the difference amounted to less than 5%. This is on the same order as the analytical precision for the Atomic Absorption method. Since somewhat more variation between runs was found in the absolute weight of particulate, the amount of vanadium collected also varied. In these preliminary trials the difference in the total amount of V inventory between runs was on the order of 20%. Considering the relatively small amount of solids collected, this difference is about as good as can be expected.

Increased combustion chamber residence time serves to promote burnout of cenospheres. Given sufficient residence time, all of the carbonaceous matter in the particle would be consumed and only ash (vanadium particles) would be emitted into the combustion product gas stream. With short residence time, i.e., high firing rate, most of the ash is retained in the cenosphere. Thus the deposits in the boiler, depending upon combustion conditions should have distinct vanadium contents. In runs 35 and 36, the solids isolated in the boiler averaged 3.54 and 3.31 wt. % V, respectively. Almost all the vanadium fallout,99%,was in the first three passes. In Runs 33 and 34, fallout in the first three passes accounted for 90% of the total deposits but 78% was in the first two passes alone. The vanadium content in these solids averaged 7.07 and 7.64 wt. % respectively or about double the previous runs. These results are summarized in Table 7.13.

Some idea of the nature of the deposits in the various boiler passes were obtained from their elemental analysis. In Table 7.14 C, H, N and S analysis of deposits from Run 33 are presented.

The solids from pass 1 and 2 which had the highest vanadium content roughly 8% (ash) also had the lowest carbon content, averaging about 53%. In passes 3 and 4 when vanadium content averaged about 4.5 wt. % (lower ash) carbon content was considerably higher and amounted to 74%. While a sulfur analysis is presented, most of the sulfur is believed to be associated with the ash as sulfate. Sulfuric acid would not be a factor since the high temperature in the passes would preclude its formation. Sulfur content appears highest in the solids containing the least amount of carbon, therefore, the most ash.

TABLE 7.13

VARIATION OF VANADIUM DISTRIBUTION IN BOILER - PRELIMINARY TESTS (ALL-VEN HIGH ASH RESID FUEL)

- FUEL FIRING RATE 1 lb./MIN

	Run 33			Run 34		
	Particulate Inventory			Particulate Inventory		
Boiler Deposits	mg/SCM	Wt.%V	ppm V	mg/SCM	Wt.% V	ppm V
Pass 1 (firetube)	40	7.5	38	42	7.8	42
Pass 2	38	8.2	32	36	9.2	42
Pass 3	18	4.3	11	21	6.2	17
Pass 4	12	4.8	9	12	4.7	7
Total	100		90	111		108

- FUEL FIRING RATE 2 LBS./MIN.

Boiler Deposits	Run 35			Run 36		
Pass 1 (firetube)	82	3.0	31	75	2.7	26
Pass 2	106	4.0	54	93	3.8	45
Pass 3	35	3.3	15	27	3.1	11
Pass 4	1	6.6	1	2	5.9	1
Total	224		101	197		83

TABLE 7.14

PARTIAL ELEMENTAL COMPOSITION OF BOILER SOLIDS (FUEL FIRING RATE 1 LB./MIN. - RUN 33)

	Elemental Composition			
Boiler Deposits	C	H	N	S
Pass 1 (firetube)	47.1	0.8	0.9	10.2
Pass 2	58.8	0.8	1.0	8.0
Pass 3	76.8	0.7	1.2	5.9
Pass 4	72.2	0.8	1.0	7.0

7.5.2 Factorial Program Results - Vanadium Recovery at High Firing Rate

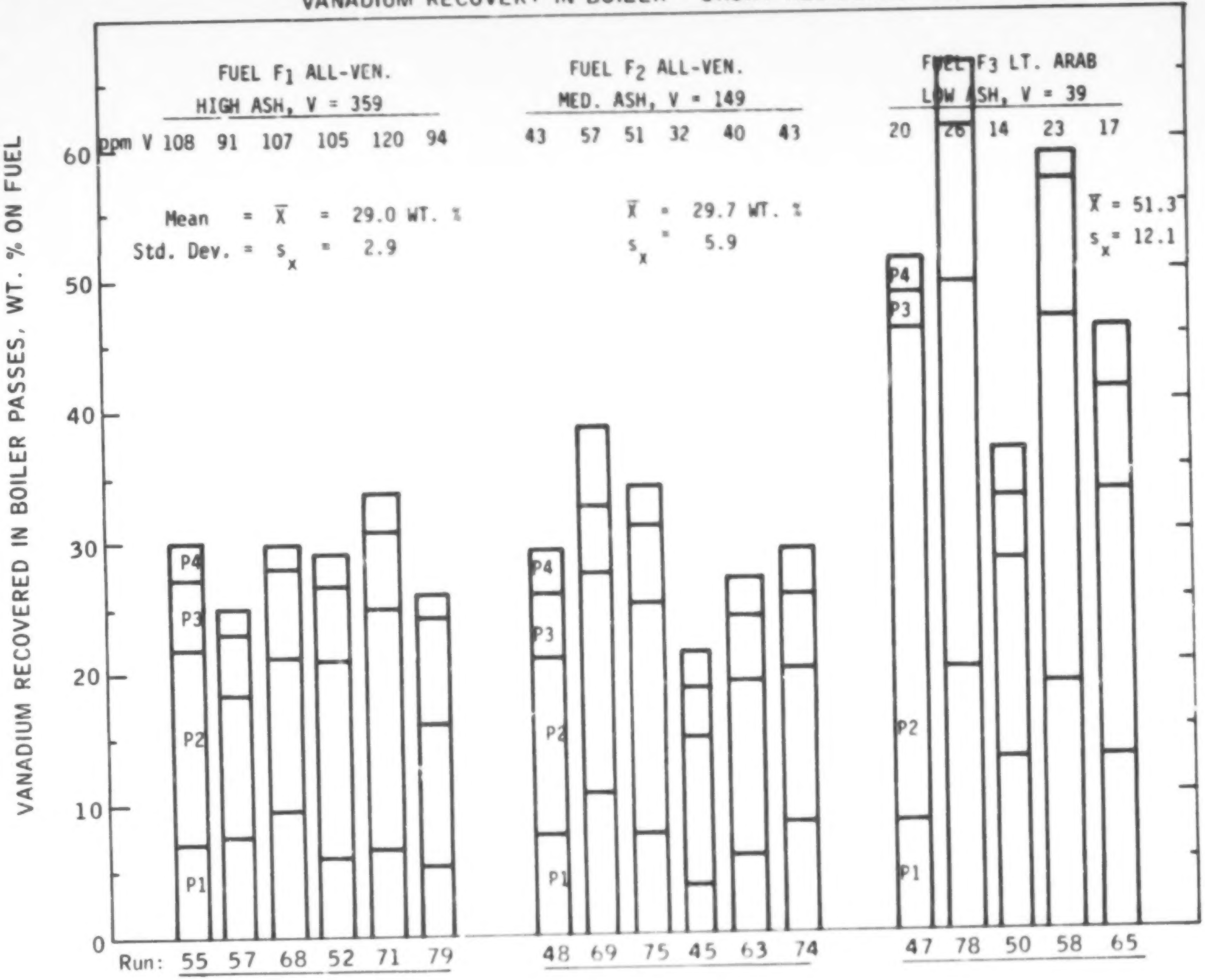
Once it was established that the tube inserts provide a reasonably consistent measure of vanadium particulate fallout in the boiler, the factorial experimental program was conducted. In each run, total vanadium was determined in the boiler solids and in each stack sampling system. In Figures 7.4 - 7.5 bar charts graphically illustrate vanadium recovery in the four passes (V recovered in boiler solids as a percent of V input from fuel) as a function of fuel type and combustion chamber residence time. Figure 7.4 summarizes the tests conducted at short residence time (τ_o), i.e. 2 lbs./min. fuel firing rate. It shows that there was no difference in percent recovery of vanadium between the high and intermediate ash all-Ven fuels. The absolute amount in the deposits, however. differed considerably because of the difference in the amount of V in the fuel oils. Over the twelve tests, recovery in the boiler tubes averaged 29.3 wt. %. Run to run fluctuations were minimal, amounting to less than 30 ppm. In contrast, vanadium recovery in the five runs made with the low ash, light Arab fuel oil averaged 51.3 wt. % of the V in the fuel and showed considerable variation between runs. This increase in variability was further indicated by the large standard deviation. In this case standard statistical techniques, i.e., F-Ratio and Bartlett's chi square tests were used to compare variability of the three groups of runs. It was established that the variances associated with the means from the all-Ven fuel oils were from the same population distribution but were different from the variance obtained in the light Arab runs.

A primary cause for the lack of repeatability in tests conducted with light Arab fuel oil was the low concentration of vanadium in the boiler solids. The V content as shown in Table 5.15 ranged from as little as a few tenths of one percent up to 2.5 wt. % but averaged about 1.0 wt. %. On the other hand, the V content of solids from the high ash all-Ven ranged from 2 wt. % to 10 wt. %, averaging 3.7 wt. %. Those from the intermediate ash all-Ven fuel varied from 2.0 wt. % to 5.5 wt. %, averaging 3.9 wt. %.

There was more particulate deposition in the boiler passes with light Arab fuel oil even though it was lower in asphaltenes (hexane insolubles) than the all-Ven fuel F_2. The all-Ven fuel F_1, had the highest asphaltene content and produced the most solid emissions. The propensity of heavy oil to form carbonaceous solids is directly

FIGURE 7.4

VANADIUM RECOVERY IN BOILER - SHORT RESIDENCE CASE



related to its asphaltene content. However, this relationship may be modified by the type and molecular weight range of these complex multi-ring structures. The light Arab fuel oil is believed to contain highly aromatic molecules which may form very refractory carbonaceous solids in the combustion chamber. The higher output of carbonaceous solids containing low ash (V) dilutes even further the concentration of vanadium in the particles.

7.5.3 Vanadium Recovery Made at Low Firing Rate

At long residence time burnout of carbonaceous material was promoted, as illustrated in Figure 7.5. Therefore, particle size was shifted toward the submicron and the relative ash content in the particles was increased. The increase of V concentration in the solids produced from the light Arab fuel improved run to run repeatability. There was no statistical difference in precision between the three groups of runs. Considering overall V recovery for the five runs on light Arab fuel, the average was 32.3 wt. % of the fuel V. This was considerably higher than the recoveries made with fuel F_1, which averaged 21.4 wt. % or fuel F_2 which averaged 24.0 wt. %. Combining the latter two, the overall average for all-Ven fuels was 22.7 wt. %, or about 40% less than for the light Arab.

The concentration of vanadium in the boiler deposits from the long residence time runs were considerably higher than obtained at short residence time. The average V content of deposits in the boiler burning the high ash all-Ven fuel (F_1) was about 9.9 wt. %. Roughly 80% of the total vanadium fallout was obtained in the first two passes while close to 95% of the total was in the first three passes. This latter value also coincided with total particulate inventory in the first three passes. At short residence time, the distribution was quite similar , 93% of the V in the boiler was recovered in the first three passes and about 95% of the particulate was obtained there.

Combustion of the intermediate ash all-Ven fuel oil resulted in deposits having an average V content of 7.6 wt. %. In this case about 90% of the V was accounted for in the first three passes along with 87 wt. % of the particulate fallout. At short residence time the distributions were similar, 90 wt. % and 89 wt. % respectively.

The light Arab fuel oil produced boiler solids which had an average V content of 2.0 wt. %. The V and total particulate distributions with this fuel were somewhat more erratic and showed less correspondence. In the first three passes approximately 87% of the V and 83% of the particulate were collected while at short residence time 93% of the V and 89% of the particulate were collected. These data are summarized in

FIGURE 7.5

VANADIUM RECOVERY IN BOILER - LONG RESIDENCE CASE

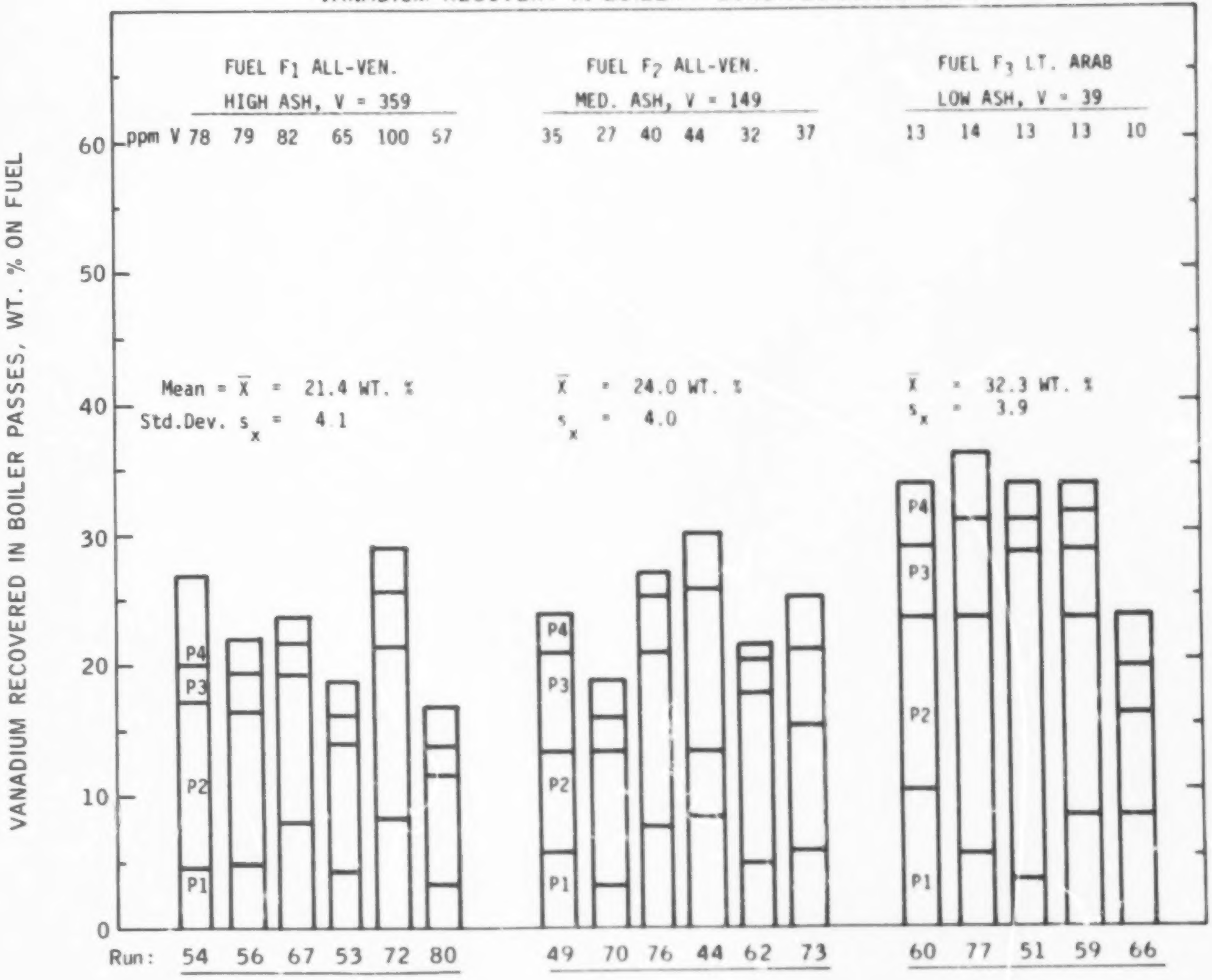


Table 7.16. While the concentration of V in the particulate obviously increases the amount of particulate actually collected is so very low that handling and work up constitute the major source of errors. This is further indicated in Run 65 where duplicate samples were analyzed for V. The largest difference between analyses was about 22%, however, the V content of the samples were quite low amounting to 0.61 wt. % and 0.75 wt. %. On the total amount of V recovered, i.e. 17 ppm the difference in analysis was only 1 ppm or about a 6% relative error.

7.5.4 Further Consideration of Total Vanadium Recovery

Regarding overall vanadium recovery at the long residence time, the fact that it was lower than at short residence time is somewhat surprising. Considering the temperature differential existing between the flue gas and heat exchanger tube surfaces and the overall length of these tubes (equivalent to a probe 40 feet long) it was thought that thermal diffusion would cause deposition of a large amount of fine particles. As previously noted in section 7.2.5 at long residence time upwards of 80% of the vanadium-bearing particulate were in the submicron size range. Since these particles had the highest V content, total recovery from the passes should have been equal to or exceeded recovery obtained at short residence time. Temperature differentials are highest between the flue gas and tube surfaces in passes 1 and 2. Therefore thermal forces would be maximized. Consistent with this mechanism at long residence time, particulate with the highest V content were deposited in the first two passes. In passes 3 and 4 the V contents of the solids were lower and more in line with the concentration found in the particulate deposited at short residence time. There was no apparent V concentration gradient in the particulate deposited in the passes at the latter combustion condition.

To determine if there was any interaction between fuels and vanadium recovery, a computer analysis of variance (ANOVA) procedure was employed. However, only the runs using the all-Ven fuels F_1 and F_2 were compared. Results from the light Arab fuel experiments were so different that these tests could not be considered as having come from the same population as the others. In Table 7.17 the analysis of variance is reproduced. Based on an F ratio test, the only significant variable affecting vanadium recovery in the boiler was residence time; fuel type had no effect.

TABLE 7.15

PARTICULATE AND VANADIUM INVENTORY IN BOILER
(LONG COMBUSTION CHAMBER RESIDENCE TIME - 0.5 LBS./MIN. F.R.)

- FUEL F_1, ALL-VEN, HIGH ASH (V = 359 PPM

	Run 54			Run 56			Run 67			Run 53			Run 72			Run 80		
Particulate Distribution	Total Particulate mg/SCM (1)	Vanadium Analysis Wt.%	Vanadium Content ppm (on fuel)	Total Part. mg/ SCM	V Anal. Wt.%	V Con-tent ppm	Total Part. mg/ SCM	V Anal. Wt.%	V Con-tent ppm	Total Part. mg/ SCM	V Anal. Wt.%	V Con-tent ppm	Total Part. ug/ SCM	V Anal. Wt.%	V Con-tent ppm	Total Part. mg/ SCM	V Anal. Wt.%	V Con-tent ppm
Boiler Solids																		
Pass 1 (firetube)	12	10.70	16	13	10.12	17	19	11.92	28	16	7.82	15	23	10.29	30	20	4.72	12
Pass 2	29	12.26	45	24	14.34	43	27	12.00	42	31	9.15	36	26	15.58	51	25	9.90	32
Pass 3	11	7.80	11	8	10.93	12	14	4.91	8	10	6.51	8	11	9.62	13	12	5.53	8
Pass 4	7	7.00	6	6	8.93	7	4	6.96	4	8	5.62	6	5	9.60	6	8	4.70	5
Total	59		78	51		79	64		82	65		65	65		100	65		57

- FUEL F_2, ALL-VEN, MEDIUM ASH, (V = 149 PPM)

Boiler Solids	Run 49			Run 70			Run 76			Run 44			Run 62			Run 73		
Pass 1 (firetube)	13	5.33	9	14	2.53	4	7	11.67	11	19	4.90	12	8	6.88	7	8	8.65	9
Pass 2	9	9.41	11	10	11.97	16	12	13.08	20	7	9.71	8	13	11.51	19	11	11.71	17
Pass 3	18	4.60	11	4	8.73	4	7	6.78	6	18	8.40	19	6	5.49	4	7	8.24	7
Pass 4	10	3.00	4	3	7.90	3	3	6.32	3	6	6.87	5	3	4.64	2	4	9.40	4
Total	50		35	31		27	29		40	50		44	30		32	30		37

- FUEL F_3, LIGHT ARAB, LOW ASH (V = 39 PPM)

Boiler Solids	Run 60			Run 7			Run 51			Run 59			Run 66		
Pass 1 (firetube)	12	2.70	4	3	5.60	2	10	0.73	1	5	4.06	3	13	1.82	3
Pass 2	19	1.91	5	24	2.17	7	22	3.48	10	18	2.54	6	20	1.82	5
Pass 3	12	1.07	2	12	1.88	3	8	0.98	1	13	1.34	2	15	0.78	1
Pass 4	6	2.62	2	7	3.29	2	8	1.05	1	11	1.29	2	11	0.85	1
Total	49		13	46		14	48		13	47		13	59		10

NOTES:

(1) All weights corrected to % O_2.

TABLE 7.16

PARTICULATE AND VANADIUM INVENTORY IN BOILER
(SHORT COMBUSTION CHAMBER RESIDENCE TIME - 2 LB./MIN. F.R.)

- **FUEL F_1, ALL-VEN, HIGH ASH (V = 359 PPM)**

	Run 55			Run 57			Run 68			Run 52			Run 71			Run 79		
Particulate Distribution	Total Particulate mg/SCM[(1)]	Vanadium Analysis Wt.%	Vanadium Content ppm (on fuel)	Total Part. mg/ SCM	V Anal. Wt.%	V Con- tent ppm	Total Part. mg/ SCM	V Anal. Wt.%	V Con- tent ppm	Total Part. mg/ SCM	V Anal. wt.%	V Con- tent ppm	Total Part. mg/ SCM	V Anal. Wt.%	V Con- tent ppm	Total Part. mg/ SCM	V Anal. Wt.%	V Con- tent ppm
Boiler Solids																		
Pass 1 (firetube)	35	5.31	24	61	3.34	26	60	4.29	33	79	2.40	24	45	4.39	25	78	1.86	19
Pass 2	81	5.19	54	148	2.12	40	69	5.15	45	117	3.58	53	102	4.93	64	145	2.11	39
Pass 3	38	4.82	23	47	3.17	19	27	6.32	22	52	2.99	20	35	4.67	21	46	4.50	27
Pass 4	8	7.10	7	11	4.44	6	7	7.38	7	19	3.33	8	8	10.06	10	13	5.42	9
Total	162		108	267		91	163		107	267		105	190		120	282		94

- **FUEL F_2, ALL-VEN, MEDIUM ASH (V = 149 PPM)**

	Run 48			Run 69			Run 75			Run 45			Run 63			Run 74		
Boiler Solids																		
Pass 1 (firetube)	23	3.85	11	23	5.45	16	28	3.22	11	19	2.07	5	20	3.68	9	21	4.43	12
Pass 2	31	5.30	21	35	5.60	25	45	4.48	26	31	4.21	17	44	3.47	19	35	3.90	18
Pass 3	15	3.59	7	21	4.66	12	24	3.50	10	17	2.86	6	23	2.94	8	20	3.43	9
Pass 4	9	3.19	4	10	2.86	4	10	3.29	4	11	2.67	4	9	3.64	4	11	2.91	4
Total	78		43	89		59	107		51	78		32	96		40	87		43

- **FUEL F_3, LIGHT ARAB, LOW ASH (V = 39 PPM)**

	Run 47			Run 78			Run 50			Run 58			Run 65[(2)]		
Boiler Solids															
Pass 1 (firetube)	28	0.76	3	36	1.67	8	36	1.02	6	22	2.55	7	22	1.59-1.69	5
Pass 2	83	1.38	15	71	1.22	11	77	0.58	6	71	1.07	10	60	1.07-1.00	8
Pass 3	37	0.29	1	39	1.02	5	35	0.53	2	39	0.75	4	35	0.61-0.75	3
Pass 4	11	0.68	1	16	1.10	2	13	0.69	1	17	1.22	2	20	0.35-0.42	1
Total	159		20	162		26	161		14	149		23	137		17

NOTES:

(1) All weights corrected to 3% O_2.

(2) Separate sample submitted under blind designation.

Vanadium recovery for the 24 runs averaged 26.0 wt. % ± 2.04 (95 percent confidence limit) of the fuel V input. The particular fuel employed did not affect vanadium recovery. Combining both residence times using fuel F_1, recovery averaged 25.2 wt. % versus 26.8 wt. % obtained with fuel F_2. On this basis, the six runs made with each fuel at the particular residence time were pooled to provide the respective total averages. Thus at short residence time, vanadium recovery averaged 29.3 wt. % ± 2.04 (95 percent confidence limit) versus 22.7 wt. % ± 2.04 (95 percent confidence limit) at long residence time. This difference of roughly 23% is statistically significant effect at the 95 percent confidence level.

The variance associated with the boiler inventory amounted to 18.97 out of the total experimental variance of 83.31 determined for the entire program. Therefore, 23% of the total variance could be explained by the variation in V recovery determined in the passes.

7.6 Recovery of Vanadium in the Stack - Summation

In each test, both stack sampling systems were operated simultaneously to prevent sample bias. For the same reason, they were alternated between the two sample ports 90 degrees apart. The four variables, i.e. sampling system, residence time, fuel and sample port location, were tested for their effect on vanadium recovery using the analysis of variance procedure (ANOVA). Since runs made with the light Arab fuel, as previously noted, gave V recoveries in many cases well over 100 percent, these tests were eliminated from the ANOVA.

The results of the analysis of variance indicated there were only two primary effects: residence time (T) which produced a change in V recovery of 10.5 units or roughly 20% and sampling systems which produced a change in recovery of about 9.3 units or 18%.

Since sample port (the flue gases were not maldistributed in the stack) and fuel type did not have an effect on vanadium recovery, tests with these variables were pooled. A two way analysis of variance using only residence time and sampling system variables was run to obtain a better estimate of experimental precision. This served as the basis for Table 7.18 which compares average vanadium recovery in the two sampling systems as a function of combustion chamber residence time. Under conditions of short residence time,

TABLE 7.17

VANADIUM RECOVERY IN THE BOILER

```
                                   ANALYSIS OF VARIANCE

SOURCE                                 SS             DF            MS              F           F.05 (Table)
                                                                                                 P(F>4.35)=0.05
ROWS (Residence Time)           0.2660004E 03      1      0.2660004E 03  0.1402333E 02    φ1=1  φ2=20

COLUMNS (Fuels F1F2)            0.1650041E 02      1      0.1650041E 02  0.8698887E 00

ROWS X COLUMNS                  0.5510421E 01      1      0.5510421E 01  0.2905051E 00

ERROR                           0.3793683E 03     20      0.1896841E 02 = VARIANCE = σ² = 18.97

            TOTAL               0.6673795E 03     23

GRAND MEAN          0.2602083E 02   = 26.0 wT% V Recovery

ERROR STD DEV       0.4355274E 01   =  4.3

  ROW MEANS
  0.2269166E 02    F1F2 T1
  0.2934999E 02    F1F2 T0

  COL MEANS
  0.2519166E 02    T1T2 F1
  0.2684999E 02    T1T2 F2
```

both sampling trains gave acceptable vanadium recovery. The Method 5 train, however, had a higher collection efficiency inventorying about 11-1/2% more vanadium than the ER&E system. When residence time was increased, both sampling systems suffered a loss in collection efficiency but the ER&E system declined the most. While the EPA train went from 59.3 wt. % down to 51.2 wt. %, a decrease of nearly 15%, the ER&E system decreased by 25%, going from 52.5 wt. % to 39.5 wt. %. At this lower level, vanadium recovery in the Method 5 train was almost 23% greater than in the ER&E system. It can be concluded from the preceding that the glass filter used in the Method 5 system is more efficient than the silicone oil-containing Greenberg-Smith impingers in collecting fine vanadium-bearing particles. It is these submicron particles which apparently pass through the last stage of the Andersen Cascade Impactor, which has a cut-off of 0.4 µm and then out the impingers and dry-ice acetone cooled condenser. The inability of the impingers to trap the very fine vanadium particulate was also evident in the EPA system. In most of the tests no more than a trace of vanadium <0.5 ppm was isolated from the chilled water impingers. In only one of the 36 runs did the amount of vanadium exceed 1 ppm and that resulted from combustion of light Arab fuel oil where about 3 ppm was found.

Regarding the Method 5 train, since there was an apparent decrease in V recovery from 59.3 wt. % to 51.2 wt. %, it was expected that downstream of the fiber glas filter a small amount of vanadium would be detected. As noted, however, there was no difference in the V content of the water impingers at either residence time. The silica gel trap backing the impingers, which is employed to dry the flue gas prior to metering, was also checked for the presence of vanadium. In Runs 72, 76 and 80 the silica gel, approximately 200 grams, was extracted with water and analyzed for V by Atomic Absorption. In all three cases, the vanadium content of the silica gel traps amounted to no more than a few ppm out of the more than 20 ppm that was missing. The uncertainty in analysis was largely due to the dilute state of the sample and subsequent high noise to signal ratio. While this amount of vanadium does not materially alter the total material balances in the three runs, it does suggest that some fine particles may be passing through the sampling system unimpeded. A check of the ER&E system was similarly attempted by submitting the contents of the oiler attached to the vacuum pump for V analysis. The results were inconclusive since here too only a few ppm V were found.

To sum up, if vanadium is passing through the sampling system as the results imply, the particles are in an extremely fine size range probably <0.1µm, and are uncollectable using standard techniques, i.e. filter, impingers and impaction devices.

TABLE 7.18

RECOVERY OF VANADIUM IN STACK SAMPLING SYSTEMS

(Basis: No statistical difference between fuel F_1 and F_2 or stack sampling location)

	EPA Method 5 Train	ER&E Train	t = Test
$\tilde{T}_0$	59.3 wt. % vanadium recovery (55.3 - 63.3)	52.5 wt. % (48.5 - 56.5)	$t = 2.02$ $\nu = 22$ $t(.025,44)$ From Table $= 1.96$
$\tilde{T}_1$	51.2 wt. % (47.2 - 55.2)	39.5 wt. % (35.5 - 43.5)	$t = 4.99$ $\nu = 22$ $t(0.025,44)$ From Table $= 1.96$

NOTE:

Experimental variance = 49.56

Std. error = $\sqrt{[illegible]/k=12}$ = 2.03

95 percent confidence interval $t(.025,44)$ = 1.96 x 2.03 $\pm \bar{X}$

Probability $-4.0 \leq \bar{X} \leq +4.0 = 0.95$

7.7 The Problem of Sulfate Formation in Water Impingers

7.7.1 Sulfuric Acid Formation

The sulfur trioxide (SO_3) content of flue gas from combustion of a typical high sulfur fuel oil burned in the Cleaver Brooks is about 20 ppm. There is sufficient water vapor present to convert this entire amount to sulfuric acid. If this occurred the acid, on condensing, would produce about 80 mg/SCM. Provided the stack temperature and gas stream are maintained above the acid dew point (280°F) condensation will not occur. Sulfur dioxide can also be converted to acid. While this reaction was thought to be slow unless a catalyst was employed, recent data published by Battelle (24) indicates that a significant part of the SO_2 in the flue gas will dissolve in the Method 5 water impingers and may oxidize over a period of several hours. The rate of oxidation is proportional to the amount of dissolved oxygen in the water. With a high sulfur fuel oil, each water impinger can dissolve as much as 20 mg SO_2/100 ml H_2O. Therefore, the oxidation of only a small amount of this will produce a measurable quantity of acid particulate. Since the potential to form significant amounts of H_2SO_4 is so high, it is not surprising that the water impingers used in the Method 5 system have been a source of varying quantities of particulate.

To overcome this problem in our Company sponsored studies, we switched from using water in the impingers to a liquid which could be heated to temperatures >350°F and in which SO_2 is insoluble. A number of experiments were run to evaluate the concept of a hot liquid impinger system as a means of overcoming the sulfate problem. Several cross comparisons were made with water impingers.

The initial evaluation was made with a sampling train consisting of a heated probe, Andersen Cascade Impactor and high velocity chilled water impingers. Under normal base load combustion conditions in the Cleaver Brook using a high sulfur fuel oil, approximately 25-30% of the particulate passed through the system and was collected in the cold water impingers. In this case about 45 mg/SCM. Approximately 90% of this material was water soluble. Analyses indicated almost an equal split between $SO_4^{=}$ tied up with metals such as V, Ni, Na, Fe and as free sulfuric acid. The acid was determined by potentiometric titration of the H^+, the sulfate by gravimetric precipitation with $BaCl_2$. On a mass basis sulfuric acid accounted for roughly 15 mg/SCM of the total impinger particulate.

With the sampling system consisting of a probe, Andersen Cascade Impactor and silicone oil in place of water impingers, particulate passing into the latter accounted for 25 wt. % of the total inventory, nearly 30 mg/SCM. Most noteworthy was the absence of sulfuric acid. Total sulfate tied up with metals in this case amounted to 16% of the impinger solids whereas in the former case, with the water impingers the amount was nearly 25% of the catch. In another modification of this experiment, a glass fiber filter was placed after the Andersen Cascade Impactor and the particulate catch in the silicone oil impingers system was measured. A small amount of particulate did pass through the filter, ∿4 wt. % of the total inventory, about 5 mg/SCM. Analysis indicated the particulate contained a small amount of sulfate but no free sulfuric acid. The weight of filter catch plus impinger material equaled 35 mg/SCM compared to the previous case of 30 mg/SCM where particulate not retained by the Andersen Impactor passed directly into the impinger system. While the weight of these particulate catches were nearly the same, the sulfate content was quite dissimilar. With the filter present in the system, sulfate comprised almost half (50%) of the solids weight compared to less than a quarter (20%) without the filter. This difference may be an indication that there was interaction between particulate retained on the filter and flue gas.

A final experiment used the Andersen Impactor, fiber glass filter and water impingers. Particulate catch from the Andersen and filter were the same as in the previous case. However, the impinger catch was much higher amounting to 20 mg/SCM compared to 5 mg/SCM with silicone oil. Based on a potentiometric titration of the H^+ about 12 mg of this total was free sulfuric acid. Other type sulfate accounted for 2 mg. These data are summarized in Table 7.19.

7.7.2 The Nature of Artificial Particulate

In the factorial study, a highly variable and unpredictable quantity of artificial particulate was isolated in each run from the chilled water impingers of the Method 5 train. These solids which consisted predominantly of ammonia and sulfate were recovered in amounts ranging from 2 to 44 mg/SCM. Attempts to correlate the formation of this material with any of the obvious variables including fuel oil sulfur content were not successful. As shown in Table 7.20 when either the light Arab (2.8 wt. % S) or intermediate ash all-Ven (1 % S) fuels were burned, a similar quantity of solids, approximately 13 mg/SCM, was isolated from the impingers. When the high ash 2.2% S fuel oil was burned, a considerably lower inventory was obtained averaging 8 ppm. Combustion chamber residence time had only a slight effect on the amount of particulate.

TABLE 7.19

COMPARISON OF PARTICULATE SULFATE/SULFURIC ACID INVENTORY

	Cascade Impactor		Cascade Impactor Plus Filter	
	Water Impingers	Silicone Oil Impingers	Water Impingers	Silicone Oil Impingers
Filter, mg/SCM				
- Sulfate	--	--	16	16
- H_2SO_4	--	--	--	--
- Total Particulate	--	--	30	30
Impingers, mg/SCM				
- Sulfate	10	5	2	0.5
- H_2SO_4	15	None	12	None
- Total Particulate	45	30	20	5

TABLE 7.20

ARTIFICIAL PARTICULATE FORMATION IN WATER IMPINGERS OF METHOD 5

	Combustion Conditions	
Fuel Type	Short Residence Time Impinger Solids, mg/SCM	Long Residence Time Impinger Solids, mg/SCM
2.2% Sulfur, High Ash (All-Ven(F_1)	8	5
1.0% Sulfur, Intermed. Ash All-Ven (F_2)	13	10
2.8% Sulfur, Low Ash, Lt Arab (F_3)	12	11

The composition of the solids isolated from the water impingers was determined for a number of runs, and is shown in Table 7.21. These solids, which were totally water soluble, contained very little ash (at 1450°F), generally less than 5 wt. %. Vanadium, which would be one of the major metallic constituents of the ash was present but in an exceedingly low concentration, ranging from 0.5 wt. % to 1.5 wt. % (expressed as V_2O_5). Carbon content of the solids was generally under 10.00 wt. %. This taken together with the low ash content tends to rule out the possibility that the material represents "real" particulate.

The major constituents of the solids are ammonia and sulfate. The latter is present in concentrations of up to 70%. In some of the preliminary runs, these artificial particulate were analyzed by X-RAY spectroscopy and found to consist of a mixture of ammonium sulfate and ammonium bisulfate exclusively. In the runs where both ammonia and sulfate analysis have been reported, the ratios also suggest a mixture of the two compounds. In several cases, the solids were dissolved in water and a standard acid-base titration was made to determine the hydrogen ion concentration. This has been converted to the equivalent amount of sulfuric acid and is reported as such in the table. The amounts generally range from 0.2 to .5 wt. %. Since the solids were dried under vacuum at 300°F for up to 8 hours, it is possible that a significant amount of free acid was removed prior to the analysis. Therefore, too much emphasis should not be placed on these titrations.

Ammonium sulfate is stable at temperatures up to 400°F. Since this material was not found in the hot silicone oil impingers but was only recovered from the water impingers of Method 5, it can be regarded as an artifact of that system. This artificial particulate would not be emitted from a boiler during combustion. Therefore, its inclusion in a particulate inventory is not corrected and will result in an erroneously high stack loading.

The presence of NH_3 in the flue gas in these runs is puzzling and has not been resolved.

7.8 Determination of Oxidation State of Vanadium Particulate in Flue Gas

A short series of experiments were run to determine the change in oxidation state of vanadium exposed to flue gas. Milligram samples of three vanadium oxides: V_2O_3 (III), V_2O_4 (V) were placed separately on a fiber glass filter, heated to 375°F and each exposed for 2 hours to flue gases produced by firing the high sulfur all-Ven heavy fuel oil with 10% excess air. Only the V_2O_5 gave any indication of reaction, changing color from mustard yellow to green. After exposure each of the samples was transferred under a nitrogen blanket into a flask and dissolved in sulfuric acid. A colorimetric determination run on the sulfuric acid solutions of the oxides indicated that approximately one third of the pentavalent vanadium (V) was reduced to tetravalent V (IV). While these experiments are by no means definitive, they do indicate that some of the vanadium in the particulate may be emitted in V^{+4} state. In a previous Company sponsored study, color changes were noted for particulate which had been collected on a hot fiber glass filter used to back up the Andersen Cascade Impactor. In that work the filter was normally taken apart in the laboratory and the particulate were, therefore, exposed to air. The fines which were usually green in color at 375°F became black or grey on cooling to ambient temperature. Subsequent reheating would not produce the reverse color change.

Since the normal vanadyl type compounds formed by V^{+4} are not volatile at stack temperatures, the presence of V^{+4} would not explain the loss of vanadium from the sampling systems.

TABLE 7.21

Composition of Solids from Method 5 Water Impingers

Run No.	Fuel	Solids Isolated, mg/SCM	V	C	H	N	NH_3	SO_4
52	High Ash - All-Ven	14	0.31	-	-	-	-	14.0
53	" " " "	9	-	-	-	-	-	27.3
54	" " " "	6	0.66	-	-	-	-	41.6
55	" " " "	8	None	5.01	2.29	8.81	-	35.0
56	" " " "	4	0.56	-	-	-	-	32.7
57	" " " "	8	0.26	-	-	-	-	25.5
67	" " " "	4	0.25	-	-	-	-	16.9
68	" " " "	10	0.14	-	-	-	1.73	13.9
71	" " " "	6	0.10	-	0.47*	-	Trace	69.76
	Intermed. Ash-All-Ven							
48	" " " "	4	None	12.29	3.65	8.65	-	23.0
49	" " " "	12	0.40	10.98	3.43	8.29	9.08	-
62	" " " "	4	Trace	-	0.22*	-	Trace	51.31
63	" " " "	5	0.20	-	0.26*	-	-	26.10
69	" " " "	11	0.83	-	-	-	9.3	40.02
	Low Ash-Lt. Arab							
46	" " " "	20	None	2.83	5.28	16.24	18.82	50.25
47	" " " "	6	1.3	4.51	3.60	8.35	2.87	32.01
50	" " " "	37	None	1.21	4.18	11.86	13.96	-
59	" " " "	11	Trace	-	0.3*	-	-	46.17
60		23	0.38	-	0.2*	-	Trace	60.62

*Reported as H_2SO_4

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APPENDIX 1

STATE OF THE ART REVIEW

VANADIUM ANALYSIS AND PARTICULATE SAMPLING METHODOLOGY

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APPENDIX 2

LABORATORY ISOLATION OF PARTICULATES COLLECTED FROM STACK SAMPLING TRAINS

APPENDIX 2

Laboratory Isolation of Particulates Collected from Stack Sampling Trains

MATERIALS

4	800 ml beakers
2	1,000 ml beaker
1	2,000 ml beaker
8	30 ml porcelain crucibles previously marked with run no. and appropriate designations. crucibles placed in furnace @ 1400°F for several hours.
1	Metler 5 decimal place balance Model H20T
1	Blackstone ultra-sonic cleaner
1	Millipore stainless steel 47 mm pressure filter holder

REAGENTS

Hexane
Isopropyl Alcohol
Dist. H_2O
Chloroform

FIRE CHAMBER

The solids accumulated in the fire chamber are swept into a teflon container then sieved through a 100 mesh screen to remove extraneous particles such as pieces of fire brick.

The two fractions, <100 and >100 are transferred to tared bottles and put into the vacuum oven to dry at 275°F for four hours. The weight is recorded and the sampler submitted for chemical analysis.

BOILER TUBE INSERTS

After completion of the warm up period, the boiler was shut down and the rear door opened. A single stainless steel tube was inserted into a randomly selected boiler tube in each of the three passes of the Cleaver Brooks Boiler. The rear door was closed and the boiler restarted. As soon as run conditions were achieved, stack sampling began. Weights of fuel at restart and at start of stack sampling and at completion of run were recorded.

The boiler tube inserts were removed and labelled as to their location in the passes.

The tubes were cleaned in the following manner; the tube insert was mounted vertically to platform with clamps and a labelled 1000 ml beaker placed under it. The tube was washed alternately with dist. H_2O and isopropyl alcohol. A plunger consisting of a rubber disc conforming to the inner diameter of the tube and mounted on a long stainless steel rod was passed up and down the length of the tube several times in order to remove any material that might adhere to the sides of the tube.

Following this the tube was again rinsed with dist. H_2O and isopropyl alcohol. The beaker was removed and put on steam bath and evaporated to a manageable volume. This was transferred to a tared and labelled crucible. Then evaporated to dryness. The solids were placed in a vacuum oven at 275°F to dry. After weighing,samples from each of the three batches of solids were submitted for vanadium analysis. In several tests, the final wash of the tubes was accomplished using about 500 ml of 0.5 NH Cl. The solution was submitted directly for V analysis.

PROBE

Cap off both ends of probe and rinse off all material that was collected on outside of the probe during run. Remove cap from nozzle tip and wash inside of nozzle and probe with dist. H_2O. When probe is full place caped end into ultra-sonic bath for approx. 30 sec. Pour into 250 ml beaker. Repeat using isopropyl alcohol. Remove cap and rinse probe from capped and directly into beaker with dis. H_2O and isopropyl alcohol.

Glass connector, probe to Andersen: Repeat same procedure used in washing probe. Rinse into 250 ml beaker containing probe wash. Place on steam bath to evaporate.

CYCLONE

Solids are recovered from cyclone using probe isolation procedure. Solids are dried under vacuum at 300°F.

ANDERSEN CASCADE IMPACTOR

8 separate stages with a corresponding stainless steel plate are washed in same manner. (The head of the Andersen is washed along with the "0" stage and plate). Carefully remove stage, wash rim and face with dist. H_2O and isopropyl alcohol into beaker. Reverse stage and repeat procedure. If any material appears to remain, use rubber policeman to remove. Remove stage and using forceps place corresponding plate into the washings, cover with water glass. Place beaker with washings and plate into ultra-sonic bath for approx. 30 sec. or until all solids are off plate. Remove plate from washings. Rinse both sides into beaker with dist. water and isopropyl alcohol. Place beaker on steam bath to evaporate.

After the last plate has been removed the base of the Andersen neck, and connector leading to the impingers will remain. They are rinsed with dist. H_2O and isopropyl alcohol into a 1,000 ml beaker marked "impinger water wash". Cover beaker and keep it aside to be used again later on in work-up.

GLASS CONNECTORS

Remove stop-cock grease. Fill connector with hexane. Cap both ends and place in ultra-sonic bath for 1 minute. Pour into 2,000 ml beaker with impinger washings. Repeat again, then rinse connectors until all traces of silicone oil are removed. Allow to dry.

FILTRATION OF SILICONE OIL

Stir oil and hexane washings in 2,000 ml beaker to be filtered. Weigh 1 millipore teflon .20 mu filter paper and place in pressure filter and lock. Add approx. 300 ml of impinger wash from beaker to sample container. Lock. Use approx. 60 psi pressure to filter. All of sample should filter in 3 hours. At end of filtration rinse sample container with 3 x 100 ml increments of hexane and pressure these through filter. When filtration is complete remove filter paper and dry in vacuum oven at 300° F for four hours. Remove filter paper, place in desicator to cool. Weigh when filter paper is at room temperature.

WATER WASH OF IMPINGERS

(This is done while impingers are filtering) check dry impingers for any traces of silicone oil. If there are traces of silicone oil, wash with hexane again adding washings to impinger sample, when there is no further trace of oil present, the dry impingers are washed with distilled water and isopropyl alcohol in the same manner as with the hexane wash. Should any trace of material remain after the water isopropyl alcohol wash an additional wash using chloroform should be used. All washings should be added to previously obtained "impinger water wash" beaker and placed on steam bath to evaporate.

WATER IMPINGERS

After removal from sampling train removal all traces of stop-cock grease from impingers. Place each impinger in ultra-sonic bath for approximately five minutes, empty contents into a 2,000 ml beaker labelled "impinger H_2O wash". Each impinger is washed by the same method; thoroughly rinse all inner surfaces of impinger, neck and arm into impinger with 100-150 ml of water. Place in ultra-sonic bath for two or three minutes. Empty into 2,000 ml "impinger wash" beaker. Repeat same procedure using isopropyl alcohol. Pour wash into beaker. If any material remains, an additional wash using chloroform is used. Evaporate contents of "impinger wash" to dryness on steam bath. Transfer material from beaker to tared 30 ml crucible using water, isopropyl alcohol as a rinse. Evaporate crucible to dryness. Place in vacuum oven at 300°F for four hours. Cool in dessicator to room temperature. Weigh and record weight on particulate emissions data sheet. Submit dry sample in screw neck vials for typical analysis.

PROBE, PLATES, IMPINGER WATER WASH SAMPLES

Weigh 30 ml crucibles and record tare weights. Transfer samples on steam bath to appropriate crucibles rinsing with water and isopropyl alcohol. Evaporate to dryness. Place in vacuum oven at 300°F. Remove crucibles, place in dessicator, weigh when crucibles are at room temperature. Record weights of all fractions on particulate emissions data sheet.

SILICONE OIL IMPINGERS

Open all impingers and wipe off stop-cock grease from ground glass joints. Place on steam bath. This will help make silicone oil less viscous and easier to handle (this can be done prior to work-up of Andersen so silicone oil will be reasonably fluid for work-up). Pour contents of all impingers into 2,000 ml beaker, rinsing with hexane. Pour approx. 250 ml hexane into each impinger. Place impinger into ultra-sonic bath for approx. 2 mins. while impinger is in ultra-sonic bath, use squeeze bottle and wash inside of impinger neck and arm into the impinger. Pour hexane into 2,000 ml beaker. Wash impinger bottle and neck thoroughly with hexane until no trace of silicone oil is present. Repeat with each impinger. Allow impingers to dry.

COMBINATION OF FRACTIONS

After all weights are recorded, samples are combined into three fractions: probe and "O"; plates 1 thru 5; plates 6,7 and impinger, and submitted for vanadium analysis by Atomic Absorption Spectroscopy. The filters, one from the filtration of the silicone oil in the ER&E train, and the fiber glass filter from the Method 5 train, after drying under vacuum at 300°F for four hours are also submitted for vanadium analysis.

ASH PROCEDURE

Using three weighing boats that have been previously heated in a furnace at 1450°F overnight and cooled to room temperature in a dessicator. Obtain tare weights on boats. Place approximately 10 mg. sample of material from each of the three fractions (dried at 500°F overnight) into the boats. Weigh and record. Place boats in furnace overnight at 1000°F. Following morning remove boats, place in dessicator to cool to room temperature. Weigh and record sample loss. Calculate ash.

COMPARISON OF TIME REQUIREMENTS FOR WORK UP OF SAMPLING SYSTEMS

EPA SYSTEM

	Prep.	Work Up*
Probe	5	10
Cyclone	5	10
Filter	15	15
Impinger	10	45
(+ Connectors)		
Leak Check	5	
Totals	40 mins.	80 mins.

Total Work Up + Prep. = 2 hours

ER&E SYSTEM

	Prep.	Work Up*
Probe + 0	5	15
Andersen 1-5	5	45
Andersen 6,7		15
Impingers (filtering)	15	210
(+ Connectors)		
Traps	15	20
Leak Check	5	-
Totals	45 mins.	305 mins.

Total Work Up + Prep.   5 Hrs. 50 mins.

*Exclusive of drying isolated solids.

APPENDIX 3

THE DETERMINATION OF VANADIUM IN PARTICULATES

APPENDIX 3

The Determination of Vanadium in Particulates

ABSORPTION SPECTROSCOPY

Scope

Atomic absorption spectroscopy is a single element technique requiring at least 3 cm^3 of sample solution per determination. Due to the small sample sizes encountered in this project only the vanadium determination was evaluated.

Sample Preparation

The solid particulate samples were dried before weighing. The dried sample was then digested with a mixture of perchloric, nitric, and sulfuric acids. This acid digestion was found to be quicker than dry ashing and is not as subject to error through loss when working with small samples.

The teflon and silica filter particulate samples were extracted with 5% HNO_3 acid. It was found that at least 99% of the vanadium is removed by this technique. Aqueous samples were analyzed directly.

Accuracy

The accuracy of an atomic absorption analysis is dependent upon the accuracy of the calibration standards, as well as physical and chemical interferences. Reagent grade $VOSO_4$, V_2O_5 and Fisher 1000 p.p.m. standards were used. Calibration standards prepared from each of these sources agreed quite well.

Several chemical species have been reported to chemically interfere with the vanadium determination. Sachaleu, Robinson, and West(1) have reported using the addition of $AlCl_3$ to overcome these interferences. This technique was therefore used for all vanadium determinations associated with this project.

The accuracy of vanadium by optical emission has been well established and was therefore used to check the atomic absorption results. Good agreement was obtained as can be seen from an inspection of Table I.

TABLE 1

COMPARISON OF VANADIUM ANALYSIS BY ATOMIC ABSORPTION AND OPTICAL EMISSION SPECTROSCOPY

Sample	wt% V	
	A. A.	O. E. S.
1	3.7	3.8
2	3.3	3.8
3	4.1	3.6
4	2.3	2.2
5	3.6	3.7
6	2.6	2.4
7	5.0	4.9
8	8.4	8.4

Sensitivity

The sensitivity of the vanadium determination is such that a minimum of 50 μg of vanadium is required per analysis. This means that a 2 mg particulate sample containing less than 2.5 wt% V could not be determined by this technique.

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(1) S. L. Sachaleu, J. W. Robinson, and P. W. West, Anal. Chim. Acta., 37 (1967) 12.

Precision

A day to day precision study was conducted using a large sample which had been sieved, dried, and thoroughly mixed. Aliquots of this sample were put through the entire procedure and the resulting sample solutions were saved. Each day a new sample solution was prepared and analyzed with previous preparations. The columns of data in Table II are the repetitive results for each sample preparation and were used to calculate the day-to-day precision of the measurement step. The top diagonal of data in Table II are the first results obtained for each new sample preparation and were used to calculate the day-to-day precision for the entire procedure. An average relative standard deviation (1σ) of 2.8% was calculated for the measurement step as compared to 4.3% for the entire procedure. These results show that the sample preparation can be carried out as precisely as the measurement.

PROCEDURE-ATOMIC ABSORPTION

Apparatus

A P&E Model 403 atomic absorption spectrometer, equipped with a vanadium hollow cathode lamp and a strip chart recorder were used in this study.

Instrumental Parameters

The following parameters apply to the P&E Model 403 unit.

Wavelength - 319.2 nm; UV setting
Lamp Current - 14 mA
Slit 4 (Spectral Band Pass - 0.2 nm)
Fuel - Acetylene
Oxidant - Nitrous oxide
Flame Stoichiometry - Reducing; red cone
1 - 1 1/2 cm in height

REAGENTS (A.A.)

Standard Vanadium Solution 1000 μg/cm^3

Available from Fisher Scientific Company.

Digestion Acid Mixture

To 150 cm^3 of conc. HNO_3 add 50 cm^3 of 72% $HClO_4$ and 180 cm^3 of conc H_2SO_4. After stirring and cooling, the solution is made up to 400 cm^3 with conc. HNO_3.

TABLE II

VANADIUM PRECISION STUDY

Date Prepared / Date Analyzed	wt. % Vanadium									
	1/21	1/22	1/24	1/30	1/31	2/11	2/13	2/21	2/24	2/25
1/21	6.58									
1/22	6.36	6.28								
1/24			6.48							
1/30	6.22	6.28		6.56						
1/31	6.46	6.28	6.71	6.36	6.39					
2/11	6.67	6.64	6.78	6.92	6.86	6.26				
2/13	6.76	6.82	6.78	6.92	6.76	6.62	7.07			
2/21	6.31	6.37	6.56	6.50	6.66	6.15	7.16	6.86		
2/24	6.62	6.64	6.56	6.74	6.80	6.50	7.25	6.95	6.84	
2/25	6.64	6.73	6.59	6.83	6.77	6.50	7.09	6.07	7.02	6.94

Aluminum Solution 3000 μg/cm^3

Weigh 6.00 g of aluminum metal into a 400 cm^3 beaker. Add 40 cm^3 of aqua regia and a few milligrams of a mercury salt. Transfer to a 2-litre volumetric flask after dissolution is complete and dilute to volume with deionized water.

Nitric Acid Solution 5% (v/v)

Add 50 cm^3 of concentrated nitric acid to a 1-litre volumetric flask and dilute to volume with deionized water.

Calibration

(1) Add 0, 1, 5, 10, and 15 cm^3 of the 1000 μg/cm^3 stock vanadium solution to each of 5-100 cm^3 volumetric flasks.

(2) Add to each of these flasks 1 cm^3 of the acid digestion mixture and 10 cm^3 of the aluminum solution. Then dilute up to volume with deionized water and mix well. This makes 0, 10, 50, 100, and 150 μg/cm^3 vanadium standards, respectively.

(3) Aspirate each of the standards into the flame using the 0 μg/cm^3 solution as the blank.

(4) Prepare a calibration curve plotted as absorbance versus μg/cm^3 vanadium.

Sample Analysis

The samples associated with this project consisted of three types: free particulate, particulate on filter paper (teflon or silica), and aqueous extract solutions.

A. Free Particulates

(1) Dry the sample for at least 1 hour at 110°C and allow to cool in a desiccator containing anhydrous magnesium perchlorate or calcium chloride as the desiccant.

(2) Weigh between 2 and 100 milligrams of sample, depending upon availability, into a 30 ml Kjeldahl digestion flask.

(3) Place the flask onto a Kjeldahl digestion rack equipped with a glass hood and bubbler system.

(4) Add 2 cm^3 of the acid digestion mixture and heat slowly until the brown fumes disappear and the solution is clear.

(5) Bring the mixture to fumes of perchloric acid and continue to heat for 15 minutes.

(6) Cool, add 5 cm^3 of water, and bring to a boil.

(7) Transfer the digestate quantitatively to a 10 cm^3 volumetric flask after cooling.

(8) Add 1 cm^3 of the aluminum solution and dilute to volume with deionized water.

(9) Measure the absorbance of the sample solution and determine the corresponding $\mu g/cm^3$ of vanadium from the calibration curve. If the absorbance is higher than the highest calibration standard, dilute to within the working range making certain that the final solution contains 300 $\mu g/cm^3$ of Al^{+3}.

(10) Calculate the wt. % vanadium using the following equation:

$$\text{wt. \% vanadium} = \frac{(\mu g/cm^3 \text{ vanadium})\ (cm^3 \text{ of final solution})\ (\text{dilution factor}) \times 10^{-1}}{\text{sample weight (milligrams)}}$$

B. Filter Samples

(1) Cut the entire filter into small pieces being careful not to lose sample and place into a 400 cm^3 beaker.

(2) Add 50 cm^3 of 5% nitric acid to the beaker.

(3) Place a watch glass over the beaker and boil for 30 minutes.

(4) Cool and filter through #1 Whatman filter paper into a 100 cm^3 volumetric flask.

(5) Add 10 cm^3 of the aluminum solution and dilute to volume with deionized water.

(6) The remainder of the sample preparation is described in steps 9 and 10 of Part A. (Free Particulates).

C. Aqueous Solutions

(1) Accurately transfer 9 cm^3 of the sample into a 10 cm^3 volumetric flask.

(2) Dilute to volume with the aluminum solution and mix well.

(3) The remainder of the sample preparation is described in steps 9 and 10 of Part A. (Free Particulates).

EMISSION SPECTROSCOPY

Scope

Emission spectroscopy is a multi-element analysis technique yielding a relative precision of at least 10%. Our existing capability at the onset of this project allowed the simultaneous determination of Ni, Fe, V, Si and Na in relatively large samples. Due to the small sample sizes to be encountered, work was done to extend the lower working limit without affecting the accuracy or precision of the method. Only solid particulate samples were studied although this technique could be extended to filter and aqueous samples.

Sample Preparation

The particulate samples were dry ashed in porcelain crucibles. The formation of a friable ash was accomplished through the addition of glycerin to the sample before ashing.

Calibration Standards

Standards consisted of the oxides of Ni, Fe, V, and Si, and NaCl. Each element was introduced into the standard to cover the low, high, and intermediate points of the range of interest. The 2.750 gm total for each standard consisted of the metal oxides, sodium chloride, and lithium tetraborate. A straight line curve was obtained for each element indicating that the amount of matrix does not produce variation in the calibration curves over the range studied. Five standards were fired to calibrate the instrument and prepare the standard curves. Scale deflection units (Y-axis) were plotted versus mgs of each element (X-axis).

The emission spectroscopy procedure is calibrated to cover the range of 0.5 to 5 mg V, 0.05 to 0.5 mg Ni, 1.00 to 25 mg Si, 1.00 to 25 mg Na, and 1.00 to 25 mg Fe.

PROCEDURE - EMISSION SPECTROSCOPY

Apparatus

Direct reading ARL Quantometer. Excitation source is a voltage spark of the ARL multisource unit, Model #4700.

ARL power driven hydraulic press with a 12.7 mm die (1/2").

Instrumental Parameters

5 sec prespark

50 sec exposure controlled by integration of a constant amount of energy from the internal standard.

Set in 10-100 scale deflection units.

Wavelengths of analytical emission lines are:

	Å
Li	4972.0 (reference line)
V	3184.0
Ni	3414.8
Si	2881.6
Na	5896.0
Fe	3020.6

Reagents

(1) Certified Spectranalyzed Glycerin.

(2) $Li_2B_4O_7$ - 4-9's pure - Spex Industries.

(3) SP-1 grade graphite - Spex Industries.

(4) Graphite rod with a flat tip - 6.35 x 50.8 mm - high purity - Spex Industries.

Procedure

(1) Weigh a minimum of 10 mg into a porcelain crucible and add 1 cm^3 of glycerin.

(2) Ash the sample at 540°C for one hour.

(3) Weigh the ash.

(4) Transfer the ash to a graphite crucible.

(5) Cover the ash with $Li_2B_4O_7$ so that the total weight of ash plus $Li_2B_4O_7$ equals 2.750 g. (Example: If ash weight is 2.0 mg add 2.748 g $Li_2B_4O_7$).

(6) Fuse at 980°C for 10 minutes.

(7) Grind the glass-like bead obtained from the fusion in a tungsten carbide mill.

(8) Sieve the ground material through a 200 mesh cloth.

(9) Blend one part of sample with two parts of SP-1 pelletizing graphite.

(10) Press a portion (∿ 1 g) into a 12.7 mm briquette with the press set at 40,000 psi.

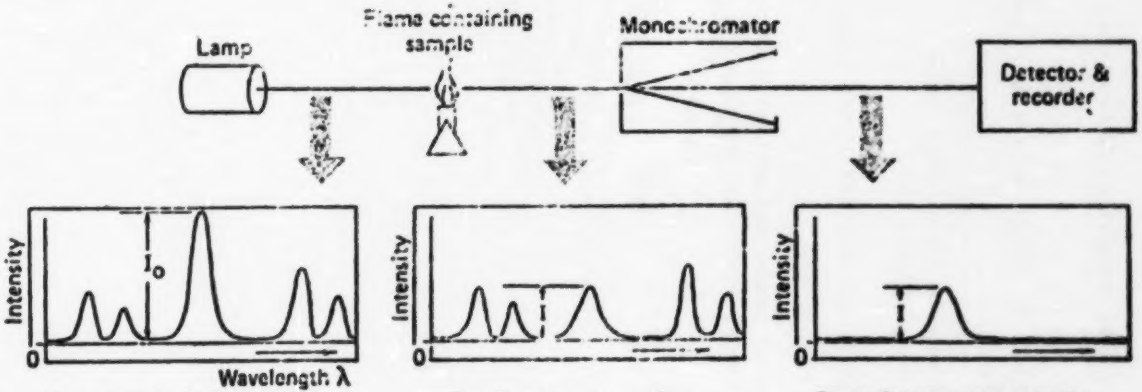
(11) Place the briquette in a brass holder. The counter electrode is a 6.35 x 50.8 mm graphite rod.

(12) Set in and fire the standards and then fire the samples on the Quantometer.

(13) Read and record scale deflection units for each element. Determine the mgs of the element from the appropriate curve.

SUMMARY OF

ATOMIC ABSORPTION SPECTROSCOPY


Lamp
Flame containing sample
Monochromator
Detector & recorder
Intensity
I_o
0
Wavelength λ
Intensity
0
Intensity
0

Hollow cathode lamp emits line spectrum of element to be determined

Resultant spectrum after absorption by sample

Photodetector sees only the resonance line, diminished by sample absorption

APPENDIX 4

OPERATIONAL DATA FROM FACTORIAL PROGRAM

APPENDIX 4

TABLE 1

EXPERIMENTAL DATA SUMMARY FOR BOILER OPERATION

Experiment No.	44	45	46	47	48	49
Fuel Type	F_2	F_2	F_3	F_3	F_2	F_2
Residence Time	τ_1	τ_0	τ_1	τ_0	τ_0	τ_1
Stack Position	2	2	1	1	1	1
Vanadium Analysis in Fuel, ppm	145	150	40	37	138	140
Operational Data						
Flue Gas Oxygen, %	2.0	2.0	2.0	2.0	2.0	2.0
Nozzle Temperature, °F	147	150	186	187	150	140
Stack Temperature, °F	213	318	220	328	318	215
Fuel Consumption, Lbs.						
• Firetube	194	450	245	579	403	99
• Heat Exchanger Inserts	111	264	172	452	262	99
• Particulate Sampling	104	237	162	362	237	74
Bacharach Smoke Tape No.	2.5	5.5	1.5	6	5.5	2.5
Boiler Deposits, grams						
Firetube	21.76	51.61	19.30	94.75	56.15	7.76
Pass 2 (1 tube of 14)	0.32	3.49	1.56	15.36	3.42	0.58
Pass 3 (1 tube of 10)	1.19	2.66	0.77	9.67	2.40	1.08
Pass 4 (1 tube of 8)	0.51	2.20	0.80	3.42	1.72	0.71
Corrected Distribution, mg/SCM (Combustion Gas)						
Firetube	19	19	14	28	23	13
Pass 2 (all tubes)	7	31	22	83	31	9
Pass 3 (all tubes)	18	17	8	37	15	18
Pass 4 (all tubes)	6	11	7	11	9	10
Total	50	78	51	159	78	50
Vanadium Analysis, Wt. %						
Firetube	4.90	2.07	2.91	0.76	3.85	5.33
Pass 2	9.71	4.21	8.81	1.38	5.30	9.41
Pass 3	8.40	2.86	3.81	0.29	3.59	4.60
Pass 4	6.87	2.67	3.64	0.68	3.19	3.00
Vanadium Distribution In Boiler Solids, ppm (on fuel)						
Firetube	12	5	5	3	11	9
Pass 2	8	17	25	15	21	11
Pass 3	19	6	4	1	7	11
Pass 4	5	4	3	1	4	4
Total	44	32	37	20	43	35
Vanadium Recovery						
Average V Content in Solids, wt. %	6.9	3.2	5.7	1.0	4.3	5.3

APPENDIX 4

TABLE 2

EXPERIMENTAL DATA SUMMARY FOR STACK SAMPLING SYSTEMS

Experiment No.	44	45	46	47	48	49
Fuel Type	F_2	F_2	F_3	F_3	F_2	F_2
Vanadium Analysis, ppm	145	150	40	37	138	140
Residence Time	τ_1	τ_0	τ_1	τ_0	τ_0	τ_1
Stack Position	2	2	1	1	1	1
ERE Sampling Train, Operating Data						
• Isokinetic Sampling Rate, %	93	99	95	93	93	96
• Sample Volume SCFDB	43.23	78.91	65.49	112.99	83.52	39.83
• Gross Particulate Weights, mg						
Probe & 0 Stage	11.79	55.51	4.82	218.38	49.05	8.90
Andersen Stages 1-5	11.99	141.67	15.39	385.48	136.44	11.03
Andersen Stages 6,7	5.13	18.30	10.95	22.09	11.60	4.89
Impingers	24.37	75.31	13.33	126.85	62.40	21.85
Total	53.28	290.79	44.49	752.80	259.49	46.67
• Vanadium Analysis, Wt. %						
Probe & 0 Stage	1.53	1.26	1.56	Trace	1.63	0.21
Andersen Stages 1-5	2.60	2.76	1.36	0.11	3.44	2.92
Andersen Stages 6,7	15.99	10.70	2.28	1.16	10.80	5.56
Impingers				6.84	13.95	15.26
• Particulate Distribution,* Wt. %						
>10μ	23	21	12	31	24	21
1-10μ	25	47	35	49	47	24
<1μ	52	32	53	20	29	55
EPA Sampling Train, Operating Data						
• Isokinetic Sampling Rate , %	98	98	1.06	92	95	1.05
• Sample Volume, SCFDB	56.60	78.91	83.70	121.26	81.34	43.26
• Gross Particulate Weights, mg						
Probe	17.56	14.05	7.11	119.88	23.31	5.10
Cyclone	2.50	54.28	3.70	209.39	38.59	1.63
Filter	59.56	221.82	52.17	459.41	190.13	50.32
Impingers	50.78	103.89	50.05	20.45	9.71	15.25
Total	130.40	394.04	113.03	809.13	261.74	72.30
• Vanadium Analysis, Wt. %						
Probe & Cyclone	2.15	1.30	0.74	0.14	1.37	Trace
Filter	14.61	6.31	7.86	1.24	7.73	15.70
Impingers	None Detected	None Detected	1.30	None Detected	None Detected	0.40

*Based on Cumulative Distribution.

APPENDIX 4

TABLE 3

EXPERIMENTAL DATA SUMMARY FOR BOILER OPERATION

Experiment No.	50	51	52	53	54	55	56	57
Fuel Type	F_3	F_3	F_1	F_1	F_1	F_1	F_1	F_1
Vanadium Analysis, ppm	39	40	350	368	350	358	358	363
Residence Time	T_0	T_1	T_0	T_1	T_1	T_0	T_1	T_0
Stack Position	2	2	2	2	1	1	1	1
Operational Data								
Flue Gas Oxygen, %	2	2	2	2	2	2	2	2
Nozzle Temperature, °F	185	178	215	205	201	205	198	200
Stack Temperature, °F	325	216	316	214	218	346	217	341
Fuel Consumption, Lbs.								
• Firetube	469	233	240	122	173	556	203	427
• Heat Exchanger Inserts	264	154	129	70	80	301	90	214
• Particulate Sampling	241	141	90	48	65	114	67	118
Bacharach Smoke Tape No.	6	2	6	2	2	5	2	5
Boiler Deposits, grams								
Firetube	102.54	13.65	108.83	10.87	11.70	111.94	14.90	148.93
Pass 2 (1 tube of 14)	8.41	1.40	6.21	0.88	0.94	10.15	0.87	13.04
Pass 3 (1 tube of 10)	5.33	0.73	3.86	0.40	0.50	6.50	0.43	5.84
Pass 4 (1 tube of 8)	2.54	0.93	1.74	0.41	0.41	1.70	0.41	1.75
Total	118.82	16.71	120.64	12.56	13.55	130.29	16.61	169.56
Corrected Distribution, mg/SCM (Combustion Gas)								
Firetube	36	10	79	15	12	35	13	61
Pass 2 (all tubes)	77	22	117	31	28	81	24	148
Pass 3 (all tubes)	35	8	52	10	11	38	8	47
Pass 4 (all tubes)	13	8	19	8	7	8	6	11
Total	161	48	267	64	58	162	51	267
Vanadium Analysis, wt. %								
Firetube	1.02	0.73	2.40	7.82	10.70	5.31	10.12	3.34
Pass 2	0.58	3.48	3.58	9.15	12.26	5.19	14.34	2.12
Pass 3	0.53	0.98	2.99	6.51	7.80	4.82	10.93	3.17
Pass 4	0.69	1.05	3.33	5.62	7.00	7.10	8.93	4.44
Vanadium Distribution in Boiler Solids, ppm (on fuel)								
Firetube	5	1	24	15	16	24	17	26
Pass 2	6	10	53	36	45	54	43	40
Pass 3	2	1	20	8	11	23	12	19
Pass 4	1	1	8	6	6	7	7	6
Total	14	13	105	65	78	108	79	91
Vandadium Recovery								
Average V Content in Solids, wt. %	0.7	2.1	3.1	8.0	10.6	5.2	12.2	2.7

APPENDIX 4
TABLE 4
EXPERIMENTAL DATA SUMMARY FOR STACK SAMPLING SYSTEMS

Experiment No.	50	51	52	53	54	55	56	57
Fuel Type	F_3	F_3	F_1	F_1	F_1	F_1	F_1	F_1
Vanadium Analysis, ppm	39	40	350	368	350	358	358	363
Residence Time	~~70~~	~~71~~	~~70~~	~~71~~	~~71~~	~~70~~	~~71~~	~~70~~
Stack Position	2	2	2	2	1	1	1	1
ERE Sampling Train, Operating Data								
• Isokinetic Sampling Rate, %	92	98	94	96	95	98	93	92
• Sample Volume, SCFDB	75	61	26	55	74	41	78	41
• Gross Particulate Weight, mg								
Probe + 0 Stage	114.5	2.8	71.6	6.1	4.9	93.8	11.4	112.5
Andersen Stages 1-5	282.9	7.6	142.7	17.6	18.4	113.5	21.0	207.4
Andersen Stages 6, 7	1 .0	19.2	26.0	16.2	22.4	9.5	24.9	13.3
Impingers	173.1	23.5	43.1	61.4	80.0	40.2	88.6	43.0
Total	484.5	53.1	283.4	101.3	125.7	257.0	145.9	376.2
• Vanadium Analysis, Wt. %								
Probe + 0 Stage	0.44	2.50	1.10	4.17	7.00	2.43	3.88	1.66
Andersen Stages 1-5	0.46	2.73	4.18	13.11	18.86	8.90	22.97	4.62
Andersen Stages 6,7	1.18	2.50	3.82	18.38	25.74	16.80	18.52	14.29
Impingers	3.28	17.76	8.25	19.09	21.77	13.12	23.71	9.31
• Particulate Distribution* , Wt. %								
>10 μ	23	6	27	6	4	35	7	32
1-10 μ	57	18	51	22	17	46	17	54
< 1 μ	20	76	22	72	79	19	76	14
EPA Sampling Train, Operating Data								
• Isokinetic Sampling Rate, %	93	105	96	96	95	105	94	105
• Sample Volume, SCFDB	86	75	34	62	79	44	84	48
• Gross Particulate Weight, mg								
Probe	30.3	3.3	57.9	3.9	4.2	45.1	9.5	43.2
Cyclone	58.4	1.7	66.7	7.4	3.3	112.9	7.3	260.3
Filter	229.0	42.4	213.6	107.0	150.5	112.6	158.5	128.7
Impingers	93.2	16.6	14.4	17.4	13.1	10.8	10.8	9.3
Tota	410.9	64.0	352.6	135.7	171.1	381.4	186.1	441.5
• Vanadium Analysis, Wt. %								
Probe + Cyclone	0.36	1.71	1.02	5.40	8.33	3.78	5.21	2.29
Filter	0.92	8.72	5.99	25.06	22.86	15.63	21.95	11.96
Impingers	None	0.43	0.31	None	0.66	None	0.56	0.26

*Based on Cumulative Distribution.

APPENDIX 4

TABLE 5

EXPERIMENTAL DATA SUMMARY FOR BOILERS

Experiment No.	58	59	60	62	63	65
Fuel Type	F_3	F_3	F_3	F_2	F_2	F_3
Vanadium Analysis, ppm	51	42	38	158	150	40
Residence Time	τ_0	τ_1	τ_1	τ_1	τ_0	τ_0
Stack Position	2	2	1	2	2	2
Operational Data						
Flue Gas Oxygen, %	2	2	2	2	2	2
Nozzle Temperature, °F	188	186	178	145	145	186
Stack Temperature, °F	357	234	218	222	341	346
Fuel Consumption, Lbs.						
• Firetube	518	267	159	213	687	667
• Heat Exchanger Inserts	264	109	75	108	325	324
• Particulate Sampling	184	55	62	48/82	178	120/160
Bacharach Smoke Tape No.	6	2	2	2	6	6
Boiler Deposits, grams						
Firetube	66.05	8.00	10.52	10.47	81.94	83.94
Pass 2 (1 tube of 14)	7.71	0.82	0.57	0.59	6.09	8.01
Pass 3 (1 tube of 10)	5.96	0.84	0.50	0.37	4.39	6.54
Pass 4 (1 tube of 8)	3.16	0.88	0.33	0.26	2.20	4.57
Total	82.88	10.54	11.92	11.59	94.62	103.06
Corrected Distribution, mg/SCM (Combustion Gas)						
Firetube	22	5	12	8	20	22
Pass 2 (all tubes)	71	18	19	13	44	60
Pass 3 (all tubes)	39	13	12	6	23	35
Pass 4 (all tubes)	17	11	6	3	9	20
Total	149	47	49	30	96	137
Vanadium Analysis, wt. %						
Firetube	2.55	4.06	2.70	6.88	3.68	1.59/1.69
Pass 2	1.07	2.54	1.91	11.51	3.47	1.07/1.00
Pass 3	0.75	1.34	1.07	5.49	2.94	0.61/0.75
Pass 4	1.22	1.29	2.62	4.64	3.64	0.35/0.42
Vanadium Distribution in Boiler Solids, ppm (on fuel)						
Firetube	7	3	4	7	9	5
Pass 2	10	6	5	19	19	8
Pass 3	4	2	2	4	8	3
Pass 4	2	2	2	2	2	2
Total	23	13	13	32	40	17
Vanadium Recovery						
Average V Content in Solids, wt. %	1.2	2.1	2.1	8.3	3.3	1.0

APPENDIX 4

TABLE 6

EXPERIMENTAL DATA SUMMARY FOR STACK SAMPLING SYSTEMS

Experiment No.	58	59	60	62	63	65
Fuel Type	F_3	F_3	F_3	F_2	F_2	F_3
Vanadium Analysis, ppm	51	42	38	158	150	40
Residence Time	$\tilde{\tau}_0$	$\tilde{\tau}_1$	$\tilde{\tau}_1$	τ_1	$\tilde{\tau}_0$	$\tilde{\tau}_0$
Stack Position	2	2	1	2	2	2
ERE Sampling Train, Operating Data						
• Isokinetic Sampling Rate, %	95	90	90	92	92	92
• Sample Volume, SCFDB	55	54	72	58	62	41
• Gross Particulate Weight, mg						
Probe + 0 Stage	100.3	10.7	4.1	7.0	48.4	55.9
Andersen Stages 1-5	164.3	6.1	7.9	8.4	138.5	130.1
Andersen Stages 6,7	13.5	2.8	4.4	9.7	13.0	8.0
Impingers	51.6	33.0	36.8	34.9	45.1	56.2
Total	329.7	52.6	53.2	60.0	245.0	250.2
• Vanadium Analysis, Wt. %						
Probe + 0 Stage	0.59	2.21	1.95	1.34	1.33	0.61/0.61
Andersen Stages 1-5	0.83	3.04	3.40	2.13	3.44	0.77/0.71
Andersen Stages 6,7	3.02	4.86	5.80	16.03	9.03	1.92/1.83
Impingers	3.34	7.14	9.58	17.33	11.00	2.09
• Particulate Distribution* , Wt. %						
>10μ	30	18	8	10	26	24
1-10μ	51	12	14	14	39	49
<1μ	19	70	78	76	35	27
EPA Sampling Train, Operating Data						
• Isokinetic Sampling Rate, %	109	91	99	95	91	97
• Sample Volume, SCFDB	73	62	82	110	61	59
• Gross Particulate Weight, mg						
Probe	104.0	8.7	5.1	6.6	50.3	69.2
Cyclone	194.4	3.7	5.0	10.6	113.7	132.0
Filter	170.7	39.9	70.0	115.1	112.4	162.2
Impingers	13.9	20.1	56.1	13.7	10.0	23.1
Total	483.0	72.4	136.2	146.0	286.4	386.5
• Vanadium Analysis, Wt. %						
Probe + Cyclone	0.69	3.54	2.35	Flask Broke	2.70	0.67/0.57
Filter	1.52	9.14	6.00	17.90	9.66	1.53
Impingers	0.65	0.76	0.09	<0.1	0.20	0.25/0.47

*Based on Cumulative Distribution.

APPENDIX 4
TABLE 7
EXPERIMENTAL DATA SUMMARY FOR BOILERS

Experiment No.	66	67	68	69	70	71	72
Fuel Type	F_3	F_1	F_1	F_2	F_2	F_1	F_1
Vanadium Analysis, ppm	38	343	363	158	158	383	335
Residence Time	τ_1	τ_1	τ_0	τ_0	τ_1	τ_0	τ_1
Stack Position	2	1	1	1	1	2	2
Operational Data							
Flue Gas Oxygen, %	2	2	2	2	2	2	2
Nozzle Temperature, °F	183	199	205	150	151	197	195
Stack Temperature, °F	219	217	354	446	218	413	220
Fuel Consumption, Lbs.							
• Firetube	202	216	296	627	222	820	197
• Heat Exchanger Inserts	91	97	296	296	66	314	102
• Particulate Sampling	69	53	152	153	56	179	91
Bacharach Smoke Tape No.	2	2	6	6	2	6	2
Boiler Deposits, grams							
Firetube	14.79	22.85	100.94	84.00	18.36	212.04	26.13
Pass 2 (1 tube of 14)	0.81	1.09	8.36	4.49	0.29	13.12	1.08
Pass 3 (1 tube of 10)	0.81	0.75	4.54	3.69	0.14	6.30	0.62
Pass 4 (1 tube of 8)	0.74	0.29	1.58	2.14	0.14	1.71	0.38
Total	17.15	24.98	115.42	94.32	18.93	233.17	28.21
Corrected Distribution, mg/SCM (Combustion Gas)							
Firetube	13	19	60	23	14	45	23
Pass 2 (all tubes)	20	27	69	36	10	102	26
Pass 3 (all tubes)	15	14	27	21	4	35	11
Pass 4 (all tubes)	11	4	7	10	3	8	5
Total	59	64	163	90	31	190	65
Vanadium Analysis, wt. %							
Firetube	1.82	11.92	4.29	5.45	2.53	4.39	10.29
Pass 2	1.82	12.00	5.15	7.34	11.97	4.93	15.58
Pass 3	0.78	4.91	6.32	4.66	8.73	4.67	9.62
Pass 4	0.85	6.96	7.38	2.86	7.90	10.06	9.60
Vanadium Distribution in Boiler Solids, ppm (on fuel)							
Firetube	3	28	33	16	4	25	30
Pass 2	5	42	45	33	16	64	51
Pass 3	1	8	22	12	4	21	13
Pass 4	1	4	7	4	3	10	6
Total	10	82	107	65	27	120	100
Vanadium Recovery							
Average V Content in Solids, wt. %	1.3	10.1	5.2	5.8	6.9	5.0	12.2

APPENDIX 4

TABLE 8

EXPERIMENTAL DATA SUMMARY FOR STACK SAMPLING SYSTEMS

Experiment No.	66	67	68	69	70	71	72
Fuel Type	F_3	F_1	F_1	F_2	F_2	F_1	F_1
Vanadium Analysis, ppm	38	343	363	158	158	383	335
Residence Time	11	11	10	10	11	10	11
Stack Position	2	1	1	1	1	2	2
ERE Sampling Train, Operating Data							
● Isokinetic Sampling Rate, %	92	92	92	99	90	91	90
● Sample Volume, SCFDB	81	64	52	52	78	57	111
● Gross Particulate Weight, mg							
Probe + 0 Stage	6.3	3.8	71.4	47.9	7.0	243.1	10.4
Andersen Stages 1-5	9.9	20.2	169.0	97.3	10.3	280.2	49.6
Andersen Stages 6,7	3.9	16.8	11.0	13.8	11.2	18.0	27.3
Impingers	50.1	87.0	80.5	46.7	57.0	79.9	125.5
Total	70.2	127.8	331.9	205.7	85.5	621.2	212.8
● Vanadium Analysis, Wt. %							
Probe + 0 Stage	0.43/0.42	1.51	2.59	2.05	5.00	2.16	6.51
Andersen Stages 1-5	2.81/2.76	12.29	7.83	3.90	10.00	5.54	18.46
Andersen Stages 6,7	5.50	24.05	17.60	9.72	15.63	15.95	28.93
Impingers	7.89	12.24	9.37	7.04	14.38	10.18	22.23
● Particulate Distribution *, Wt. %							
>10μ	9	4	24	22	8	42	5
1-10μ	13	16	50	49	12	42	23
<1μ	78	80	26	29	80	16	72
EPA Sampling Train, Operating Data							
● Isokinetic Sampling Rate, %	99	103	90	99	95	100	102
● Sample Voluem SCFDB	92	73	51	52	84	63	126
● Gross Particulate Weight, mg							
Probe	4.4	9.2	19.8	30.1	3.8	105.2	8.5
Cyclone	2.6	6.1	135.9	76.5	1.5	415.9	9.6
Filter	71.8	151.1	153.6	110.1	104.8	170.8	120.1
Impingers	9.1	7.7	15.8	16.9	19.9	11.3	15.1
Total	87.9	174.1	325.1	233.6	130.0	703.2	153.3
● Vanadium Analysis, Wt. %							
Probe + Cyclone	1.82/1.67	5.00	4.50	1.80	2.50	2.87	5.71
Filter	6.27	17.74	14.85	8.72	13.11	13.00	26.65
Impingers	0.13/0.14	0.25	0.14	0.83	0.25	<0.1	0.63

*Based on Cumulative Distribution.

APPENDIX 4

TABLE 9

EXPERIMENTAL DATA SUMMARY FOR BOILERS

Experiment No.	73	74	75	76	77	78	79	80
Fuel Type	F_2	F_2	F_2	F_2	F_3	F_3	F_1	F_1
Vanadium Analysis, ppm	150	150	150	145	38	38	365	373
Residence Time	$\tilde{\tau}_1$	$\tilde{\tau}_0$	$\tilde{\tau}_0$	$\tilde{\tau}_1$	$\tilde{\tau}_1$	$\tilde{\tau}_0$	$\tilde{\tau}_0$	$\tilde{\tau}_2$
Stack Position	2	2	1	1	1	1	2	2
Operational Data								
Flue Gas Oxygen, %	2	2	2	2	2	2	2	2
Nozzle Temperature, °F	150	150	150	150	185	185	200	202
Stack Temperature, °F	238	455	410	225	219	391	384	219
Fuel Consumption, Lbs.								
• Firetube	199	662	378	209	174	482	463	198
• Heat Exchanger Inserts	88	358	207	91	98	196	191	84
• Particulate Sampling	66	252	117	78	89	119	115	63
Bacharach Smoke Tape No.	2	6	6	2	2	6	6	2
Boiler Deposits, grams								
Firetube	9.06	83.55	63.22	9.08	2.70	100.85	207.56	22.85
Pass 2 (1 tube of 14)	0.42	5.36	4.02	0.47	0.98	5.72	11.40	0.86
Pass 3 (1 tube of 10)	0.35	4.32	2.91	0.35	0.66	4.37	5.00	0.57
Pass 4 (1 tube of 8)	0.25	2.99	1.50	0.23	0.46	2.30	1.78	0.47
Total	10.08	96.22	71.65	10.13	4.80	113.24	225.74	24.75
Corrected Distribution, mg/SCM (Combustion Gas)								
Firetube	8	21	28	7	3	36	78	20
Pass 2 (all tubes)	11	35	45	12	24	71	145	25
Pass 3 (all tubes)	7	20	24	7	12	39	46	12
Pass 4 (all tubes)	4	11	10	3	7	16	13	8
Total	30	87	107	29	46	162	282	65
Vanadium Analysis, wt. %								
Firetube	8.65	4.43	3.22	11.67	5.60	1.67	1.86	4.72
Pass 2	11.71	3.90	4.48	13.08	2.17	1.22	2.11	9.90
Pass 3	8.24	3.43	3.50	6.78	1.88	1.02	4.50	5.53
Pass 4	9.40	2.91	3.29	6.32	3.29	1.10	5.42	4.70
Vanadium Distribution in Boiler Solids, ppm (on fuel)								
Firetube	9	12	11	11	2	8	19	12
Pass 2	17	18	26	20	7	11	39	32
Pass 3	7	9	10	6	3	5	27	8
Pass 4	4	4	4	3	2	2	9	5
Vanadium Recovery Total	37	43	51	40	14	26	94	57
Average V Content in Solids, wt. %	9.8	3.8	3.7	10.7	2.4	1.2	2.6	6.9

APPENDIX 4

TABLE 10

EXPERIMENTAL DATA SUMMARY

Experiment No.	73	74	75	76	77	78	79	80
Fuel Type	F_2	F_2	F_2	F_2	F_3	F_3	F_1	F_1
Vanadium Analysis, ppm	150	150	150	145	38	38	365	373
Residence Time	τ_1	τ_0	τ_0	τ_1	τ_1	τ_0	τ_0	τ_1
Stack Position	2	2	1	1	1	1	2	2
ER&E Sampling Train, Operating Data								
● Isokinetic Sampling Rate, %	95	92	97	96	94	99	95	93
● Sample Volume, SCFDB	79	83	42	101	112	42	42	78
● Gross Particulate Weight(uncorrected),Mg								
Probe + 0 Stage	5.0	57.6	45.6	4.0	8.7	72.9	165.1	8.2
Andersen Stages 1-5	9.3	142.9	82.5	13.8	25.1	126.6	218.8	30.4
Andersen Stages 6,7	9.7	25.3	10.9	7.7	6.1	12.8	18.4	17.8
Impingers	58.7	87.4	39.9	67.0	44.8	66.9	52.7	87.4
Total	82.7	313.2	178.9	92.5	84.7	279.2	455.0	143.8
● Vanadium Analysis, wt. %								
Probe + 0 Stage	3.27	1.99	1.89	2.41	1.76	0.63	1.27	3.16
Andersen Stages 1-5	12.70	3.05	3.59	8.23	2.76	0.80	3.20	8.99
Andersen Stages 6,7	17.38	8.29	5.56	10.50	6.46	1.56	7.55	14.63
Impingers	16.29	6.66	8.44	18.70	13.96	2.21	9.20	20.11
● Particulate Distribution* wt. %								
>10µ	6	18	29	5	12	26	40	6
1-10µ	14	46	42	14	27	45	44	18
<1µ	80	36	29	81	61	29	16	76
EPA Sampling Train, Operating Data								
● Isokinetic Sampling Rate, %	96	97	98	98	102	101	100	100
● Sample Volume, SCFDB	90	86	42	104	122	43	44	83
● Gross Particulate Weight (uncorrected), mg								
Probe	7.0	29.0	22.6	3.3	5.2	43.6	66.2	8.2
Cyclone	3.1	49.9	64.8	13.9	15.5	96.8	271.6	29.9
Filter	82.5	156.0	91.5	100.0	95.4	130.1	156.1	161.6
Impingers	4.3	20.7	5.0	12.8	5.5	5.1	7.3	6.6
Total	96.9	255.6	183.9	130.0	121.6	275.6	501.2	206.3
Vanadium Analysis, wt. %								
Probe + Cyclone	3.47	1.86	2.11	2.96	1.88	0.59	1.35	1.79
Filter	21.71	6.60	9.18	19.60	7.10	15.22	9.18	20.57
Impingers	1.18	0.09	0.83	2.50	0.49	1.41	0.28	0.64

*Based on Cumulative Distribution.

APPENDIX 5

PARTICULATE INVENTORY AND VANADIUM BALANCE
(All data corrected to 3% O_2 in flue gas)

TABLE 1

Particulate Inventory and Vanadium Balance From Combustion of High Ash Venezuelan Resid
(Short Combustion Chamber Residence Time)

Particulate Distribution		Run 55			Run 57			Run 52		
		Total Particulates mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on Fuel)	Total Particulates mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on Fuel)	Total Particulates mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on Fuel)
Boiler Solids										
Pass 1 (firetube)		35	5.31	24	61	3.34	26	79	2.40	24
Pass 2		81	5.19	54	148	2.12	40	117	3.58	53
Pass 3		38	4.82	23	47	3.17	19	52	2.99	20
Pass 4		8	7.10	7	11	4.44	6	19	3.33	8
	Total	162		108	267		91	267		105
Stack Particulate										
• ER&E Train										
>10μ		75	2.43	23	99	1.66	21	97	1.10	14
1-10μ		97	8.90	110	167	4.62	98	183	4.18	97
<1μ		39	14.53	72	43	12.87	71	79	7.37	74
	Total	211		205	309		190	359		185
• EPA Train										
Probe & Cyclone		123	3.78	59	215	2.29	63	128	1.02	17
Filter		86	15.63	171	91	1.96	138	214	5.99	163
		(209)			(306)			(342)		
Water Impingers		8	-	-	7	0.26	Trace	14	0.31	Trace
	Total	217		230	313		201	356		180

TABLE 2

Particulate Inventory and Vanadium Balance From Combustion of High Ash Venezuelan Resid (Short Combustion Chamber Residence Time)

		Run 68			Run 71			Run 79		
Particulate Distribution		Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Particulate mg/SCM	Vanadium Analysis Wt.%	Vanadium Content ppm (on fuel)
Boiler Solids										
Pass 1 (firetube)		60	4.29	33	45	4.39	25	78	1.86	19
Pass 2		69	5.15	45	102	4.93	64	145	2.11	39
Pass 3		27	6.32	22	35	4.67	21	46	4.50	27
Pass 4		7	7.38	7	8	10.06	10	13	5,42	9
	Total	163		107	190		120	282		94
Stack Particulate										
• ER&E Train										
>10μ		55	2.59	18	152	2.16	42	144	1.27	23
1-10μ		115	7.83	115	152	5.54	108	158	3.20	64
<1μ		60	10.24	78	58	11.08	82	58	8.52	63
	Total	230		211	362		232	360		150
• EPA Train										
Probe & Cyclone		102	4.50	58	280	2.87	102	256	1.35	44
Filter		101	14.85	191	92	13.00	152	118	9.18	138
		(203)			(372)			(374)		
Water Impingers		10	0.14	Trace	6	<0.10	Trace	6	0.38	Trace
	Total	213		249	378		254	380		182

TABLE 3
Particulate Inventory and Vanadium Balance From Combustion of High Ash Venezuelan Resid
(Long Combustion Chamber Residence Time)

Particulate Distribution		Run 54			Run 56			Run 53		
		Total Particulates mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on Fuel)	Total Particulates mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on Fuel)	Total Particulates mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on Fuel)
Boiler Solids										
Pass 1 (firetube)		12	10.70	16	13	10.12	17	16	7.82	15
Pass 2		29	12.26	45	24	14.34	43	31	9.15	36
Pass 3		11	7.80	11	8	10.93	12	10	6.51	8
Pass 4		7	7.00	6	6	8.93	7	8	5.62	6
	Total	59		78	51		79	65		65
Stack Particulate										
• ER&E Train										
>10μ		2	7.00	2	4	3.88	2	4	4.17	2
1-10μ		10	18.86	23	11	22.97	31	14	13.11	23
<1μ		45	23.35	133	47	22.83	137	44	20.16	114
	Total	57		158	62		170	62		139
• EPA Train										
Probe & Cyclone		3	8.33	3	7	5.21	4	6	5.40	4
Filter		64	22.86	186	63	21.95	177	58	25.06	184
		(67)			(70)			(64)		
Water Impingers		22	0.66	Trace	4	0.56	Trace	9	-	-
	Total	89		189	74		181	73		188

TABLE 4

Particulate Inventory and Vanadium Balance From Combustion of High Ash Venezuelan Resid
(Long Combustion Chamber Residence Time)

Particulate Distribution		Run 67			Run 72			Run 80		
		Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm (on fuel)
Boiler Solids										
Pass 1 (firetube)		19	11.92	28	23	10.29	30	20	4.72	12
Pass 2		27	12.00	42	26	15.58	51	25	9.90	32
Pass 3		14	4.91	8	11	9.62	13	12	5.53	8
Pass 4		4	6.96	4	5	9.60	6	8	4,70	5
	Total	64		82	65		100	65		57
Stack Particulate										
• ER&E Train										
>10μ		3	1.51	1	3	6.51	3	4	3.16	2
1-10μ		11	12.29	17	15	18.46	35	11	8.99	13
<1μ		54	14.38	98	46	23.33	137	47	18.53	111
	Total	68		116	64		175	62		126
• EPA Train										
Probe & Cyclone		7	5.00	4	5	5.71	3	15	1.79	3
Filter		70	17.74	159	67*	24.65	100	65	20.57	170
		(77)			72 (37)			(80)		
Water Impingers		4	0.25	Trace	4	0.63	Trace	3	0.64	Trace
	Total	81		163	76		103	83		173

*Average of Runs 53 and 80.

TABLE 5

Particulate Inventory and Vanadium Balance From Combustion of Intermediate Ash Venezuelan Resid
(Short Residence Time Case)

	Run 45, Fuel F_2			Run 48, Fuel F_2			Run 63		
Particulate Distribution	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (On fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)
Boiler Solids									
Pass 1 (firetube)	19	2.07	5	23	3.85	11	20	3.68	9
Pass 2	31	4.21	17	31	5.30	21	44	3.47	19
Pass 3	17	2.86	6	15	3.59	7	23	2.94	8
Pass 4	11	2.67	4	9	3.19	4	9	3.64	4
Total	78		32	78		43	96		40
Stack Particulate									
• ER&E Train									
>10μ	26	1.26	4	26	1.63	5	34	1.33	6
1-10μ	58	2.76	20	51	3.44	22	51	3.44	22
<1μ	40	10.70	54	31	13.42	53	46	7.18	42
Total	124		78	108		80	131		70
• EPA Train									
Probe & Cyclone	29	1.30	5	24	1.37	4	88	2.70	30
Filter	95	6.31	76	77	7.73	76	62	9.66	76
	(124)			(101)			(150)		
Water Impingers	44	Trace	-	4	Trace	-	5	0.20	Trace
	168		81	105		80	155		106

TABLE 6

Particulate Inventory and Vanadium Balance From Combustion of Intermediate Ash Containing Venezuelan Resid (Short Residence Time Case)

	Run 69			Run 74			Run 75		
Particulate Distribution	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)
Boiler Solids									
Pass 1 (firetube)	23	5.45	16	21	4.43	12	28	3.22	11
Pass 2	36	7.34	33	35	3.90	18	45	4.48	26
Pass 3	21	4.66	12	20	3.43	9	24	3.50	10
Pass 4	10	2.86	4	11	2.91	4	10	3.29	4
Total	90		65	87		43	107		51
Stack Particulate									
• ER&E Train									
>10μ	29	2.05	8	23	1.99	6	41	1.89	10
1-10μ	65	3.90	32	58	3.05	23	59	3.59	27
<1μ	39	7.6	38	45	7.15	41	41	7.65	40
Total	133		78	126		70	141		77
• EPA Train									
Probe & Cyclone	69	1.80	16	31	1.86	7	69	2.11	18
Filter	71	8.72	79	62	6.60	52	72	9.18	84
	(140)			(93)			(141)		
Water Impingers	11	0.83	1	8	0.09	Trace	4	0.83	<1
Total	151		96	101		59	145		102

TABLE 7

Particulate Inventory and Vanadium Balance From Combustion of Intermediate Ash Venezueland Resid
(Long Residence Time Case)

	Run 44, Fuel F_2			Run 49, Fuel F_2			Run 62		
Particulate Distribution	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)
Boiler Solids									
Pass 1 (firetube)	19	4.90	12	13	Na	-	8	6.88	7
Pass 2	7	9.71	8	9	Na	-	13	11.51	19
Pass 3	18	8.40	19	18	Na	-	6	5.49	4
Pass 4	6	6.87	5	10	3.00	4	3	4.64	2
Total	50		44	50		Est. (44)	30		32
Stack Particulate									
• ER&E Train									
>10μ	9	1.53	2	8	0.21	Trace	3	1.34	1
1-10μ	10	2.60	3	10	2.92	4	5	2.13	1
<1μ	22	15.99	44	22	14.10	39	26	16.61	55
Total	41		49	40		43	34		57
• EPA Train									
Probe & Cyclone	12	2.15	3	5	-	-	5	Flask Broke	-
Filter	36	14.61	66	39	15.70	79	35	17.90	80
	(48)			(44)			(40)		
Water Impingers	30	-	-	12	-	-	4	<0.1	Trace
Total	78		69	56		79	44		80

TABLE 8

Particulate Inventory and Vanadium Balance From Combustion of Intermediate Ash Venezuelan Resid
(Long Residence Time Case)

	Run 70			Run 73			Run 76		
Particulate Distribution	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)
Boiler Solids									
Pass 1 (firetube)	14	2.53	4	8	8.65	9	7	11.67	11
Pass 2	10	11.97	16	11	11.71	17	12	13.08	20
Pass 3	4	8.73	4	7	8.24	7	7	6.78	6
Pass 4	3	7.90	3	4	9.40	4	3	6.32	3
Total	31		27	30		37	29		40
Stack Particulate									
• ER&E Train									
>10	3	5.00	2	2	3.27	1	2	2.41	1
1-10	4	10.00	6	5	12.70	8	4	8.23	5
<1	29	14.9	55	28	16.82	60	25	17.58	56
Total	36		63	35		69	31		62
• EPA Train									
Probe & Cyclone	2	2.50	1	4	3.47	2	6	2.96	2
Filter	42	13.11	70	31	21.71	86	33	19.60	81
	(44)			(35)			(39)		
Water Impingers	8	0.25	Trace	2	1.18	<1	4	2.50	1
Total	52		71	37		88	43		84

TABLE 9

Particulate Inventory and Vanadium Balance From Combustion of Low Ash Light Arab Resid
(Short Residence Time Case)

	Run 47			Run 50			Run 58		
Particulate Distribution	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm (on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)
Boiler Solids									
Pass 1 (firetube)	28	0.76	3	36	1.02	5	22	2.55	7
Pass 2	83	1.38	15	77	0.58	6	71	1.07	10
Pass 3	37	0.29	1	35	0.53	2	39	0.75	4
Pass 4	11	0.68	1	13	0.69	1	17	1.22	2
Total	159		20	161		14	149		23
Stack Particulate									
• ER&E Train									
>10μ	69	Trace	-	50	0.44	3	59	0.59	4
1-10μ	109	0.11	2	123	0.46	7	101	0.83	11
<1μ	45	6.84	34	43	2.90	16	38	5.23	25
Total	223		36	216		26	198		40
• EPA Train									
Probe & Cyclone	90	0.14	2	35	0.36	2	140	0.69	12
Filter	128	1.24	20	90	0.92	11	79	1.52	15
	(218)			(125)					
Water Impingers	6	-	-	37	-	-	6	0.65	Trace
Total	224		22	162		13	225		27

TABLE 10

Particulate Inventory and Vanadium Balance From Combustion of Low Ash Light Arab Resid
(Short Residence Time Case)

Particulate Distribution	Run 65 Total Particulate mg/SCM	Run 65 Vanadium Analysis Wt. %	Run 65 Vanadium Content ppm (on fuel)	Run 78 Total Particulate mg/SCM	Run 78 Vanadium Analysis Wt. %	Run 78 Vanadium Content ppm (on fuel)
Boiler Solids		Duplicate[1]	Average			
Pass 1 (firetube)	22	1.59 - 1.69	5	36	1.67	8
Pass 2	60	1.07 - 1.00	8	71	1.22	11
Pass 3	35	0.61 - 0.75	3	39	1.02	5
Pass 4	20	0.35 - 0.42	1	16	1.10	2
Total	137		17	162		26
Stack Particulate						
• ER&E Train						
>10μ	48	0.67 - 0.61	4	58	0.63	4
1-10μ	98	0.77 - 0.71	9	100	0.80	10
<1μ	54	2.3	16	64	2.08	17
Total	200		29	222		31
• EPA Train						
Probe & Cyclone	115	0.67 - 0.57	9	109	0.59	8
Filter	93	1.53	18	101	15.22	20
	(208)			(210)		
Water Impingers	13	0.25 - 0.47	Trace	4	1.41	<1
Total	221		27	214		28

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[1] Separate samples submitted under blind designation.

TABLE 11

Particulate Inventory and Vanadium Balance From Combustion of Low Ash Light Arab Resid

(Long Residence Time Case)

	Run 46			Run 59			Run 60		
Particulate Distribution	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm(on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)	Total Part. mg/SCM	V Anal. Wt. %	V Cont. ppm (on fuel)
Boiler Solids									
Pass 1 (firetube)	14	2.94	5	5	4.06	3	12	2.70	4
Pass 2	22	8.81	25	18	2.54	6	19	1.91	5
Pass 3	8	3.81	4	13	1.34	2	12	1.07	2
Pass 4	7	3.64	3	11	1.29	2	6	2.62	2
Total	51		37	47		13	49		13
Stack Particulate									
• ER&E Train									
>10μ	3	1.56	<1	6	2.21	2	2	1.95	<1
1-10μ	8	1.36	1	4	3.04	1	4	3.40	2
<1μ	12	2.28	4	23	10.67	31	19	9.35	23
Total	23		5	33		34	25		25
• EPA Train									
Probe & Cyclone	4	Trace	-	6	3.54	3	4	2.35	1
Filter	21	7.86	21	22	9.14	25	29	6.00	22
	(25)			(28)			(33)		
Water Impingers	20	1.30	3	11	0.76	1	23	0.10	Trace
Total	45		34	39		29	56		23

TABLE 12

Particulate Inventory and Vanadium Balance From Combustion of Low Ash Light Arab Resid (Long Residence Time Case)

	Run 66			Run 77		
Particulate Distribution	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm (on fuel)	Total Particulate mg/SCM	Vanadium Analysis Wt. %	Vanadium Content ppm (on fuel)
Boiler Solids						
Pass 1 (firetube)	13	1.82	3	3	5.60	2
Pass 2	20	1.82	5	24	2.17	7
Pass 3	15	0.78	1	12	1.88	3
Pass 4	11	0.85	1	7	3.29	2
Total	59		10	46		14
Stack Particulate						
• ER&E Train						
>10μ	3	0.43	<1	3	1.76	1
1-10μ	4	2.81	1	7	2.76	2
<1μ	23	7.6	22	16	12.26	25
Total	30		23	26		28
• EPA Train						
Probe & Cyclone	3	1.82	1	6	1.88	1
Filter	26	6.27	21	26	7.10	24
	(29)			(32)		
Water Impingers	3	0.13	Trace	2	0.49	Trace
Total	32		22	34		25

APPENDIX 6

CONVERSION FACTORS

ENGLISH TO METRIC UNITS

To Convert From	To	Multiply By
°F	°C	(°F -32) 5/9
"H_2O	mm Hg	1.8682
ft^3	m^3	0.02832
lbs/min	Kg/min	0.45359
Inches	mm	25.4
Btu/lbs	Kcal/Kg	0.555
Feet	Meters	0.30480